

AIR POLLUTION CONTROL BY USING ADVANCED OXIDATION PROCESSES (AOPs)

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ABSTRACT

Among air pollution control strategies, air cleaning with Advanced Oxidation Processes (AOPs) has been drawing more and more attention because of the restraints in the production of secondary pollution. AOPs have a wide range of applications such as air (odour elimination, purification), soil (remediation) and water decontamination. Ideally, the photo catalyst, titanium dioxide, is introduced in the top layer of the concrete pavement for best results. In addition, the combination of TiO₂ with cement-based products offers some synergistic advantages, as the reaction products can be adsorbed at the surface and subsequently be washed away by rain. The main aim of this research work is to measure the effect of titanium dioxide as photo catalyst in purifying nitrogen oxide (NO_x) and Carbon Oxides (CO_x) on pavement surface and outdoor environment condition. For that, TiO₂ is replaced for cement at different proportions of 5%, 10% & 15% in terms of weight in the cement concrete moulds of 10 mm uniform thickness and curing is done for seven days, then same were exposed to the sunlight at Ijoor circle sampling point Rama Nagar Town for 21 days of observation. From the Energy Dispersive Spectroscopy (EDS) analysis, result it is observed that atom percentage increased maximum of 59.05 for carbon atoms for 10% proportion specimen. Then, check the amount of percentage for carbon atoms adsorbed by 10% proportion specimen at police/Kandaya Bhavan circle and Railway station circle sampling points of Rama Nagar Town for 21 days of observations and the results shows that, carbon atom percentage increased maximum of 42.99 and 58.69 for carbon atoms respectively at above sampling points. From this work, it is conclude that the Carbon atoms and Nitrogen atoms present in the atmosphere will be reduce up to some level when replace 10% of Titanium dioxide with cement in the concrete moulds of 10 mm thickness by Photo catalytic activity.

Key words: Advanced Oxidation Processes (AOPs), Titanium dioxide, photo catalyst, atmosphere, Carbon oxides ; Energy Dispersive Spectroscopy (EDS).

1. INTRODUCTION

“Quality of life” is becoming a main issue in modern urban environments. Comfort, mobility, energy resources and respect for the environment are key points of interest in future developments. Behind the rapid development of the society due to urbanization and industrialization all over the world including in the past decades, many environmental problems have arisen, especially the air pollution caused by different kinds of chemical generally produced from human activities. [2]

Even if humans stop combusting fossil fuels and discharging CO₂ into the atmosphere, the average global temperature of the Earth will continue to increase for the rest of the century for several reasons. Firstly, the long lifetime of CO₂ (estimated in the 100- 300 year range) means that the excess atmospheric stocks (515 Gt Carbon) would continue to drive radiative forcing and global warming for many decades [7]. The main emissions caused by motor traffic are nitrogen oxides (NO_x), hydrocarbons (HC), sulphur dioxide (SO₂) and carbon monoxide (CO).

Air pollution control, the techniques employed to reduce or eliminate the emission into the atmosphere of substances that can harm the environment or human health. Air is considered to be polluted when it contains certain substances in concentrations high enough and for durations long enough to cause harm or undesirable effects. The atmosphere is susceptible to pollution from natural sources as well as from anthropogenic activities.

There have been many attempts to reduce emissions. However, there are still emissions polluting the air to a significant level. A method of removing these pollutants at the street level once they are emitted to the atmosphere is an attractive air quality management [3]. A solution for the air pollution by traffic can be found in the treatment of the pollutants as close to the source as possible [4].

Many technologies have been developed for air pollutants removal and continue to be developed. Photocatalysis, as a promising technology developed, is defined as the process by which various environmental pollutants are degraded on the surface of a semiconductor photo-catalyst when exposed to a sufficiently energetic irradiation source, and is an important group of AOPs. AOPs rely on in-situ production of highly reactive hydroxyl radicals ($\cdot\text{OH}$). Hydroxyl radicals are produced with the help of one or more primary oxidants (e.g. ozone, hydrogen peroxide, oxygen) and/or energy sources (e.g. ultraviolet light) or catalysts (e.g. titanium dioxide). Because, this method is easier to implement than common ones, less costly, fast reaction at ambient operating conditions and can achieve high yields. In addition, photocatalytic oxidation systems can be cleaned without the requirement of extra chemicals. When all these properties are taken into consideration, the photocatalytic oxidation process is the most reasonable method that can be preferred for air pollutant removal [8].

Photo catalysts, when activated by light are capable of supporting chemical reactions which can degrade certain atmospheric pollutants, e.g. NO_x and volatile organic compounds (VOCs), as well as non-volatile compounds degrade into organic residues. This latter property is associated with the easy removal of dirt and gives the familiar “self-cleaning”, or more correctly “easy-cleaning” property.

The photocatalytic degradation of NO_x and CO_x from field studies has been measured by two techniques: (i) by measuring the reduction of the ambient air pollution, which is difficult to estimate when, in the reference site the NO_x and CO_x concentration is highly variable; or (ii) by measuring the by-products created by the degradation process on the photo-catalyst surface [7]

This study attempts to find out the amount of NO_x and CO_x absorbed by measuring the by-products created by the degradation process on the photo-catalyst concrete pavement surface having different proportion of TiO_2 at high traffic density areas.

2. TITANIUM DIOXIDE (TiO_2)

Titanium dioxide is one of the basic materials in everyday life. It has been widely used as white pigment in paints, cosmetics and food stuffs. There are indeed good reasons for favouring TiO_2 nano materials as the semiconductor of our choice in this document, due to its superior characteristics, such as ability to be coated as a thin film on a substrate. Studies conducted to identify the effect of substrate on NO_x degradation via heterogeneous photocatalysis suggest that titanium dioxide films are greatly affected by the substrate material and it is concluded that the mortar substrate exhibited high efficiency when compare to any other substrate [6]. Oxidation eliminates, like (TiO_2) photo catalyst has received significant interest in recent years due to its fascinating properties, such as electronic, optical, and UV absorption. Recently, photocatalytic oxidation has been shown to be a promising and effective technology for pollution control [1]. The definition of photocatalysis is: “Change in the rate of a chemical reaction or its initiation under the action of ultra-violet, visible, or infrared radiation in the presence of a substance the photo-catalyst that absorb slight and is involved in the chemical trans-formation of the reaction partners.” [7]. TiO_2 is the most commonly used photo-catalysts with a band gap of 3.2 eV (wavelength $\lambda < 388 \text{ nm}$).

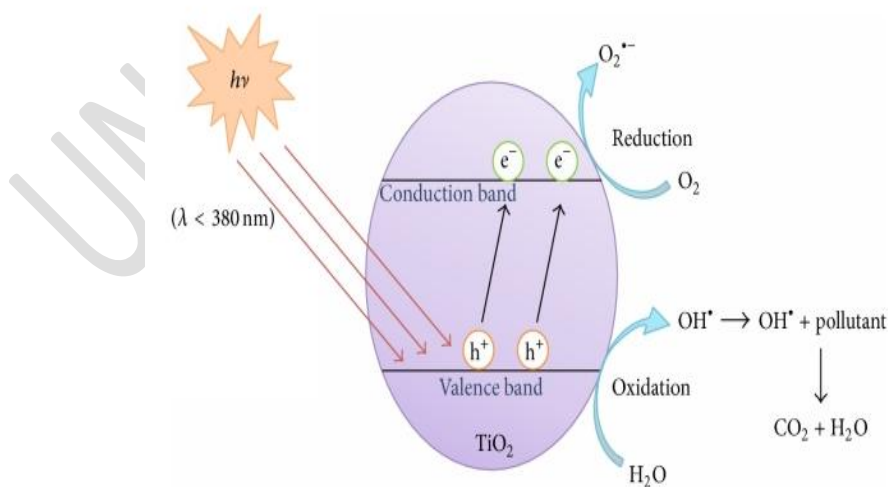
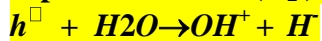


Image 1: Photocatalysis

Source: [5]

Photocatalysis, a process that occurs at the surface of a semi-conductor exposed to light. When a photon with energy equal to or larger than the band gap of the semiconductor is absorbed, an electron (e-) from the valence band is promoted to the conduction band. It results in the presence of a “hole” in the valence band (h+). The h+ and e- are strong oxidizing and reducing agents, respectively. The electron-hole pair may react with electron donors or acceptors adsorbed on the semi-conductor surface. If reaction does not occur, the electron-hole pair recombines and the energy is dissipated as heat. Oxygen and water, adsorbed at the semi-conductor surface, are catalyzed to form reactive species, superoxide anion (O₂⁻) and hydroxyl radical (OH⁺):



Hydroxyl radicals and superoxide anions are strong oxidizing and reducing agents, respectively. They can react with pollutant molecules adsorbed to the photocatalytic surface, such as NO_x or hydrocarbons, to form Nitric Acid, carboxylic acids, or carbon dioxide [3].

3. MATERIAL AND METHODS

The materials used in this study are highlighted as follows.

3.1 Cement;- The 53 grade ordinary Portland cement complying to Indian standards is used throughout the investigation.

3.2 Water:-Water free from pollutants and hardness is used for mixing and the curing was done with the same.

3.3 Fine aggregates:- Locally available river sand of specific gravity 2.68 and fineness modulus 4.58 conforming to zone II were used throughout the investigation for all concrete mixes.

3.4 Course aggregate;- Course aggregate having a size of 10 mm to 4.75 mm and specific gravity 2.74 were used throughout the investigation for all concrete mix.

3.5 Titanium Dioxide:- Titanium dioxide, also known as titanium (IV) oxide or titania, is the naturally occurring oxide of titanium, chemical formula TiO₂. Titanium oxides may be made into the nanoparticle size (0.2100nanometers). TiO₂content: 94.5% min. Specification resistance: 8000 ohm meter. pH: 6.0. Whiteness: 96.8%.

Titanium dioxide mixed with concrete at different concentration for preparation of mould and placed at all sampling points. TiO₂ is blended with cement at different proportions like 5%, 10%, 15% by weight and it is uniformly coated with a thickness of 10 mm on 300 mm X 200 mm size concrete specimen surface and water curing is done for 7 days. The prepared specimens are exposed to the sunlight in high density traffic area i.e Ijoor circle, Ramanagar for duration of 21 days. Then the specimens were tested by using Energy Dispersive Spectroscopy (EDS) instrument and from that find out the percentage of titanium replaced at different concentration of different elements atom particles on the surface before and after weathering activities.

From the literature, it is observed that maximum amount of pollutants i.e., carbon atoms are absorbed at 10% of titanium dioxide replacement. The optimum percentage of replacement of titanium dioxide specimens are prepared and placed at different high density traffic areas like Railway station circle and Police Bhavana circle, Ramanagar (Figure 1) for 21 days and once again find out the amount of pollutants atom absorbed.



Figure 1. Map showing the sampling points at Ramanagar Town

4. RESULTS AND DISCUSSION

The amount of pollutants absorbed from different percentage of titanium dioxide replacement to cement at Ijoor sampling point are analysed by using EDS and results were tabulated and discuss below.

4.1. Initial EDS Report For 5% of Titanium Dioxide

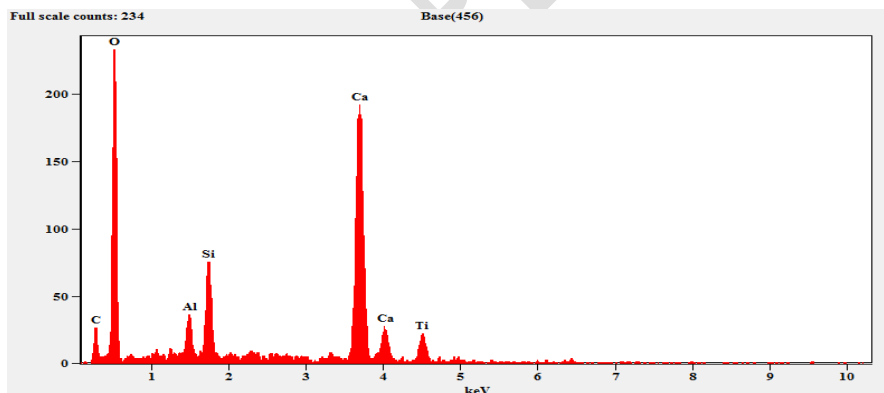
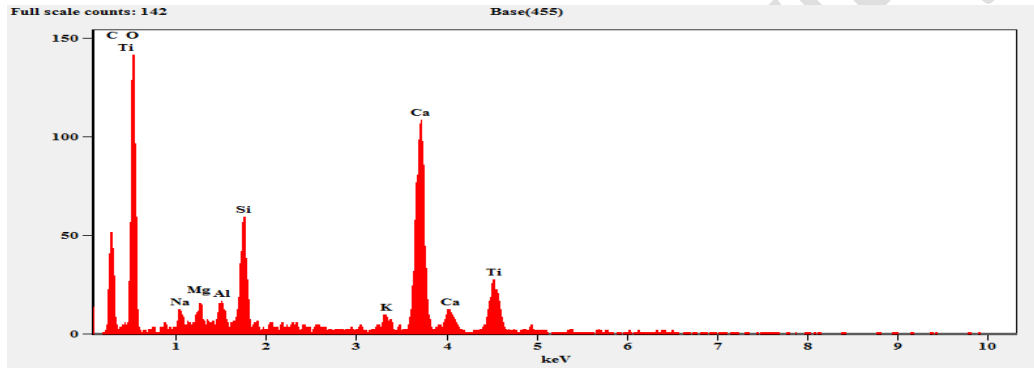


Figure 2. Initial EDS report for 5% replacement of titanium dioxide

Table 1. Initial EDS Quantitative result for 5% replacement of titanium dioxide

<i>Element Line</i>	<i>Weight %</i>	<i>Weight % Error</i>	<i>Atom %</i>
<i>C</i>	33.80	± 1.88	59.52
<i>O</i>	4.29S	---	5.67
<i>Al</i>	3.59	± 0.27	2.81
<i>Si</i>	7.84	± 0.51	5.90
<i>Ca</i>	44.06	± 1.32	23.25
<i>Ti</i>	6.42	± 1.01	2.84

4.2. EDS Report For 5% of Titanium Dioxide after 21 Days



Figur 3. EDS report for 5% replacement of titanium dioxide after 21 days.

Table 2. EDS Quantitative result for 5% replacement of titanium dioxide after 21 days.

<i>Element Line</i>	<i>Weight %</i>	<i>Weight % Error</i>	<i>Atom %</i>
<i>C</i>	49.78	± 1.88	72.13
<i>O</i>	7.03S	± 3.92	7.64
<i>Na</i>	1.98	± 0.38	1.50
<i>Mg</i>	1.36	± 0.23	0.98
<i>Al</i>	1.22	± 0.22	0.79
<i>Si</i>	4.98	± 0.40	3.09
<i>K</i>	1.39	± 0.22	0.62
<i>Ca</i>	21.74	± 0.99	9.44
<i>Ti</i>	10.52	± 0.65	3.82

4.3. Initial EDS Report For 10% of Titanium Dioxide

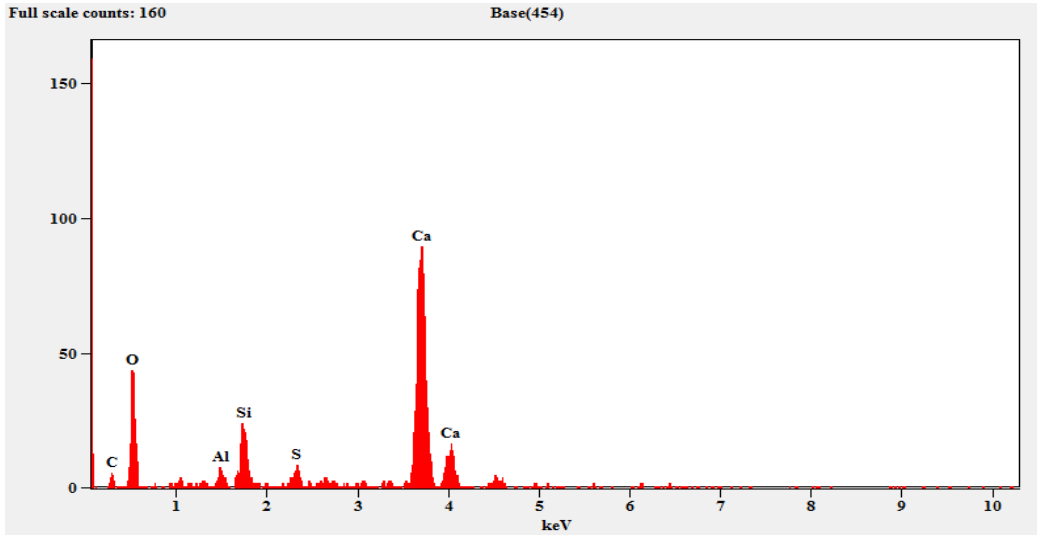


Figure 4. Initial EDS report for 10% replacement of titanium dioxide

Table 3. Initial EDS Quantitative result for 10% replacement of titanium dioxide

<i>Element Line</i>	<i>Weight %</i>	<i>Weight % Error</i>	<i>Atom %</i>
<i>C</i>	7.76	± 1.41	13.44
<i>O</i>	47.43	± 3.22	61.69
<i>Al</i>	1.35	± 0.24	1.04
<i>Si</i>	4.59	± 0.49	3.40
<i>S</i>	1.82	± 0.25	1.18
<i>Ca</i>	37.05	± 1.53	19.24

4.4. EDS Report For 10% of Titanium Dioxide After 21 Days

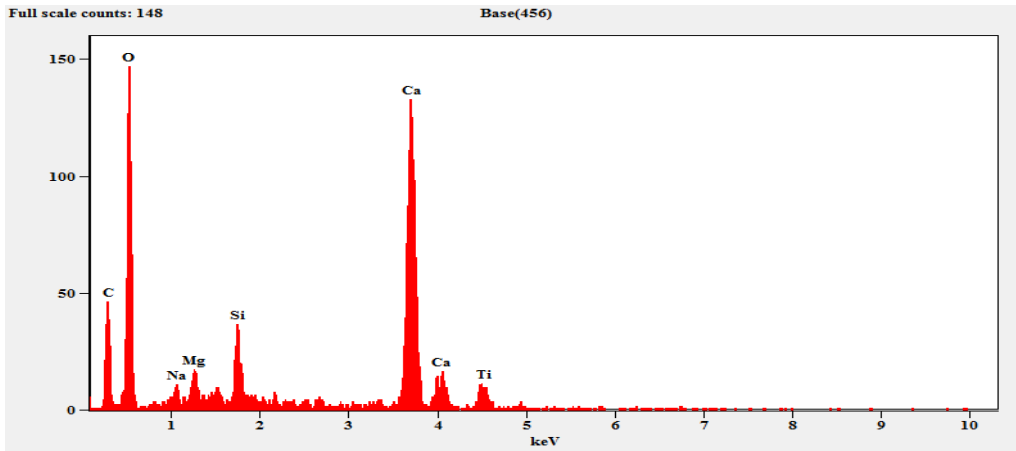


Figure 5. EDS report for 10% replacement of titanium dioxide after 21 days.

Table 4. EDS Quantitative result for 10% replacement of titanium dioxide after 21 days

<i>Element Line</i>	<i>Weight %</i>	<i>Weight % Error</i>	<i>Atom %</i>
<i>C</i>	48.24	± 1.97	72.49
<i>O</i>	3.80S	± 5.02	4.29
<i>Na</i>	2.53	± 0.47	1.99
<i>Mg</i>	2.17	± 0.27	1.61
<i>Si</i>	2.90	± 0.45	1.86
<i>Ca</i>	34.66	± 1.24	15.61
<i>Ti</i>	5.70	± 0.57	2.15

4.5. Initial EDS Report For 15% of Titanium Dioxide

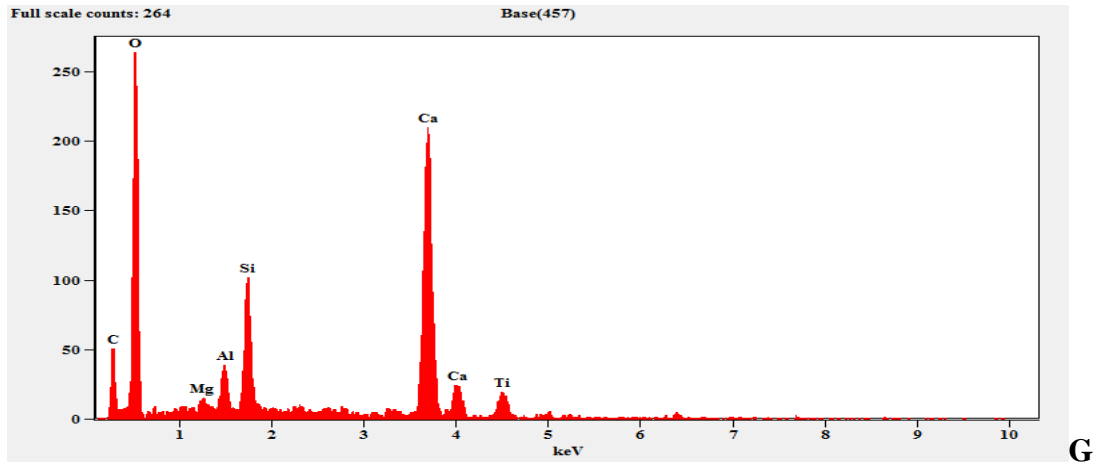


Figure 6. Initial EDS report for 15% replacement of titanium dioxide.

Table 5. Initial EDS Quantitative result for 15% replacement of titanium dioxide

<i>Element Line</i>	<i>Weight %</i>	<i>Weight % Error</i>	<i>Atom %</i>
<i>C</i>	43.30	± 1.82	68.25
<i>O</i>	4.18S	---	4.94
<i>Mg</i>	1.02	± 0.20	0.79
<i>Al</i>	2.95	± 0.22	2.07
<i>Si</i>	7.36	± 0.44	4.96
<i>Ca</i>	34.95	± 1.04	16.51
<i>Ti</i>	6.25	± 0.47	2.47

4.6. EDS Report For 15% of Titanium Dioxide after 21 Days

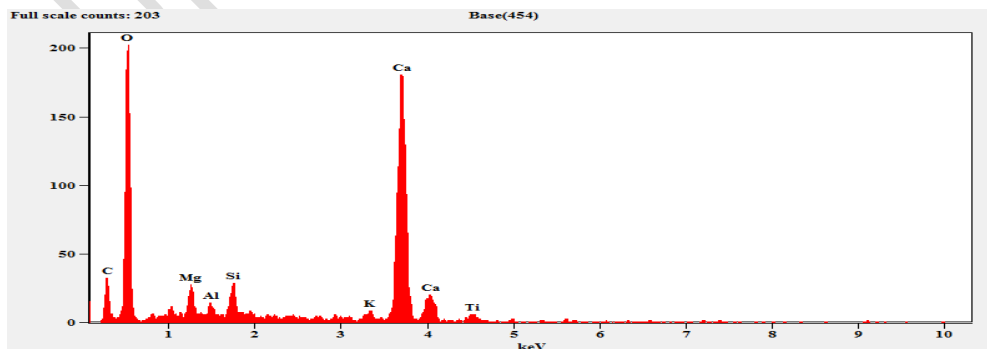


Figure 7. EDS report for 15% replacement of titanium dioxide after 21 days

Table 6. EDS Quantitative result for 15% replacement of titanium dioxide after 21 days

<i>Element Line</i>	<i>Weight %</i>	<i>Weight % Error</i>	<i>Atom %</i>
<i>C</i>	36.75	± 1.85	63.73
<i>O</i>	1.73S	± 5.36	2.25
<i>Mg</i>	3.57	± 0.34	3.06
<i>Al</i>	1.31	± 0.27	1.01
<i>Si</i>	3.22	± 0.29	2.38
<i>K</i>	1.58	± 0.25	0.84
<i>Ca</i>	49.24	± 1.53	25.59
<i>Ti</i>	2.59	± 0.53	1.13

4.7. EDS Report For 10% Of Titanium Dioxide After 21 Days at Kandaya/Police Bhavan Sampling point

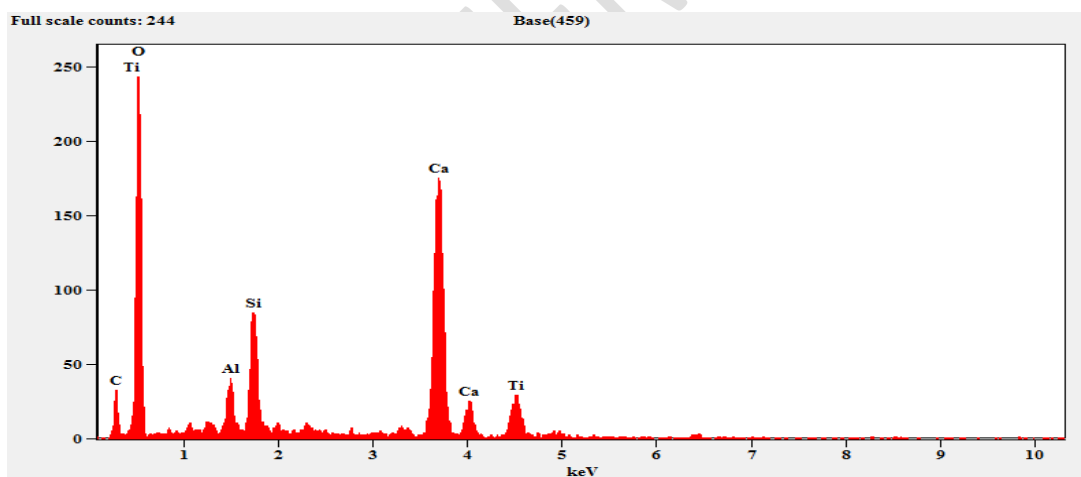


Figure 8. EDS report for 10% replacement of titanium dioxide after 21 days

Table 7. EDS Quantitative result for 10% replacement of titanium dioxide after 21 days

<i>Element Line</i>	<i>Weight %</i>	<i>Weight % Error</i>	<i>Atom %</i>
<i>C</i>	32.05	± 1.75	56.46
<i>O</i>	7.52S	---	9.95
<i>Al</i>	3.74	± 0.27	2.93
<i>Si</i>	7.59	± 0.51	5.72
<i>Ca</i>	37.82	± 1.14	19.97
<i>Ti</i>	11.26	± 0.66	4.98

4.8. EDS Report For 10% Of Titanium Dioxide After 21 Days at Railway Station Circle Sampling point

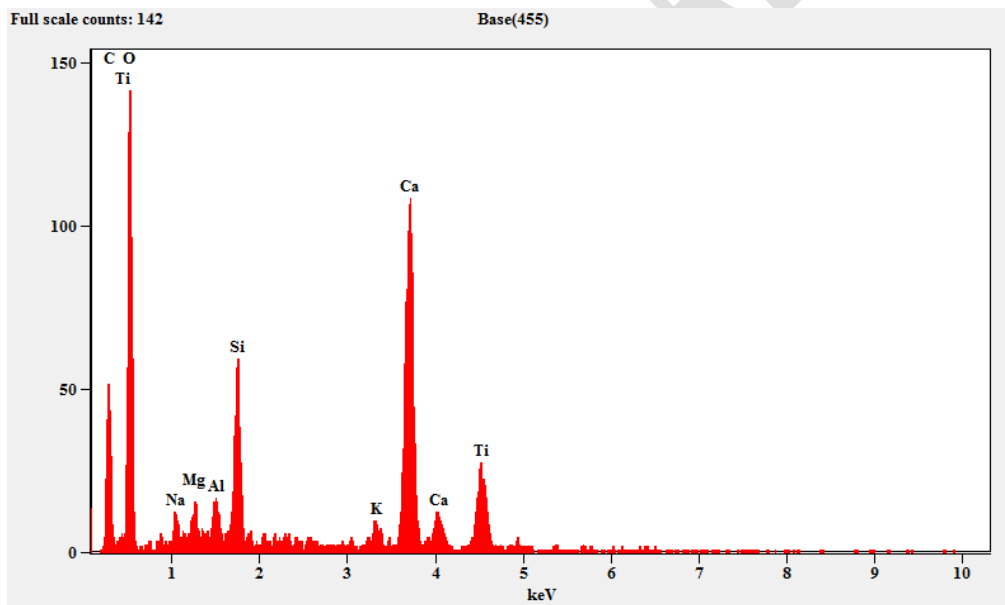


Figure 9. EDS report for 10% replacement of titanium dioxide after 21 days

Table 8. EDS Quantitative result for 10% replacement of titanium dioxide after 21 days

<i>Element Line</i>	<i>Weight %</i>	<i>Weight % Error</i>	<i>Atom %</i>
<i>C</i>	49.78	± 1.88	72.13
<i>O</i>	7.03S	± 3.92	7.64
<i>Na</i>	1.98	± 0.38	1.50
<i>Mg</i>	1.36	± 0.23	0.98
<i>Al</i>	1.22	± 0.22	0.79
<i>Si</i>	4.98	± 0.40	3.09
<i>K</i>	1.39	± 0.22	0.62
<i>Ca</i>	21.74	± 0.99	9.44
<i>Ti</i>	10.52	± 0.65	3.82

Table 9. Percentage of carbon atoms absorb by specimens of 5%, 10% and 15% TiO₂ replacement for cement on concrete pavement surface.

Sl No	Description			
		5	10	15
1	% of TIO2 replace			
2	Initial Carbon atom present in %	59.52	13.44	68.25
3	Amount of carbon atom present after 21 days in% at Ijoor circle	72.13	72.49	63.73
4	% amount of carbon atom increased/decreased after 21 days at Ijoor Circle	12.61	59.05	4.52
5	Amount of carbon atom present after 21 days in% at Railway station sample	----	72.13	----
6	% of carbon atom increased after 21 days at Railway station sample	----	58.69	----
7	Amount of carbon atom present after 21 days in% at Police Bhavana sample	----	56.46	----
8	% of carbon atom increased after 21 days at Police Bhavana sample	---	42.99	---

From the above table 8 it was observed that at 5% replacement specimen is having ability to absorbed 12.61 % of carbon atoms from the atmosphere at Ijoor circle sampling point. Similarly 10% and 15% replacement specimens were having ability to absorbed 59.05% and 4.72% of carbon atoms respectively. Therefore, From this analysis it is evident that 10% replacement of cement with titanium dioxide gives

better pollution absorption capacity when compare with the 5% and 15% replacement specimens. Hence 10% concentration of titanium dioxide replacement to cement were moulded and placed at top of the pavement surface at Railway station circle and police/kandaya bhavan circle sampling points for 21 days and then analyzed by using EDS and the results shows that, presence of carbon atom percentage increased maximum of 42.99 and 58.69 respectively at above sampling points.

From the table 8 it is observed that % of carbon atom is increased after 21 days since, Photocatalytic processes will takes place due to the presence of TiO₂ on the pavement surface by that carbon present in the atmosphere is converted into carbon atoms and it is deposited on the specimen that indicates some amount of CO_x pollutants were will absorbed from the atmosphere by the TiO₂.

5. CONCLUSION

The usage of Advanced Oxidation Processes (AOPs) for air pollutants removal is an emerging technique. Photocatalytic oxidation process has several advantages when it is compared with traditional treatment methods such as cost effective, production of less harmful by-products, ease of operation. On the basis of results obtained in this work, it is concluded that mixing TiO₂ with pavements could reduce harmful emissions CO_x at street level and benefit a cleaner living environment for the public. In this research work the absorbance of NO_x is not identified in the EDS analysis, since absorbance may be in a trace amount in the study area because the specimen exposure time is only for 21 days.

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