Visible Light Photocatalytic Degradation of Nitrogen Dioxide using Zinc Ferrite Titania as Photocatalyst

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Abstract— Visible light photocatalytic degradation of nitrogen dioxide was studied using zinc ferrite titania as photocatalyst. A photocatalytic reactor was made up of concrete block and glass was fabricated for studying photocatalytic oxidation of NO_2 under visible light. Zinc ferrite titania was prepared and it's particle size and band gap energy was found out by X-Ray Diffraction (XRD) study and Ultraviolet – Diffusive Reflectance Spectrometry (UV-DRS) respectively. Catalyst was coated on the concrete block surface and NO_2 was produced and pumped in to the reactor which was equipped with visible light source. Effect of catalyst dosage, irradiation time, light intensity and initial concentration of NO_2 were studied in lab scale and optimum catalyst dosage and irradiation time was found to be 10 mg/cm^2 and 20 minutes respectively. The maximum removal efficiency was found to be 84% at optimum conditions. It was observed that removal efficiency of nitrogen dioxide increases as the light intensity increases and decreases as the initial concentration increases. Performance of zinc ferrite titania catalyzed photodegradation was evaluated in the field under direct sunlight and ambient NO_2. Average removal efficiency of ambient NO_2 was found to be 81% in the field

Keywords—: Visible Light, NO_2 degradation, photocatalysis, zinc ferrite titania

I. INTRODUCTION

Nitrogen dioxide (NO_2) is an irritant gas which at high concentration has harmful effect on health and environment. Nitrogen oxides (NOx) are the generic term for a group of highly reactive gases, most of them emitted in air in the form of nitric oxide (NO) and nitrogen dioxide (NO_2). Nitrogen oxides are for instance formed when fuel is burnt at high temperatures, as it is the case in combustion processes in automobiles. Various studies have been conducted for controlling NO_2 concentration, like adsorption using activated carbon, biological treatment, photocatalytic conversion in automobiles etc. The photocatalyst such as Titanium dioxide (TiO_2) has been used for removing NO_2 in presence of UV light [11].

Dalton et al. (2001) reported that the TiO_2 activated by ultra violet light can be used for the removal of harmful nitrogen oxides by oxidation to nitrates. Huang et.al (2010) conducted study on photocatalytic oxidation of nitrogen oxides using platinum doped TiO_2 be activated by visible light. But the cost of platinum was major drawback. Tseng et.al (2011) conducted study on nickel doped TiO_2 for photocatalytic oxidation of nitrogen oxides. But the efficiency

obtained was only 33%. Ballari et.al (2010) had studied degradation of nitrogen oxides by concrete paving stones containing TiO_2. But TiO_2 can be activated only by UV light. Zinc ferrite is a semiconductor (bandgap 1.9 eV) that has potential application in the conversion of sunlight. However, because of the lower valence band potential and poor property in photoelectric conversion, zinc ferrite cannot be used directly in the photocatalytic destruction of toxic organic compounds. Titania has high photoactivity and superior property in photoelectric conversion, while zinc ferrite is sensitive to visible light. So coupling of these two semiconductors may become a new type of composite having high utility of sunlight, high photoactivity and high efficiency of photoelectric conversion [7]. The development of such high efficient photocatalyst and its application on structures may make better results in reduction of NO_2 concentration. Therefore, photocatalytic degradation of nitrogen dioxide has been studied under visible light irradiation under zinc ferrite titania as photocatalyst was coated on concrete surface.

II. EXPERIMENTAL

A. Development of Photocatalytic Reactor For No_2 Removal

The photocatalytic reactor developed for the lab scale study is shown in Fig. 1. Photocatalytic reactor (30cm*25cm*10cm) was designed as a box shaped structure which is made up of two cement blocks (25cm*10cm*3cm) as vertical wall, one concrete base (30cm*25cm*3cm) and glass plates. It is a simple model of a road section in which vertical concrete blocks resembles structures like walls on either side of roads or dividers or any vertical structures where the photocatalyst can be coated for the degradation of NO_2. The base part was made of concrete. The other three sides are covered with light transmitting glasses. The reactor was placed inside a wooden compartment (60cm*45cm*45cm).Two tungsten lamps each of 200W intensity and wavelength of 465 nm was fixed in the wooden compartment facing each other and the reactor was placed at the centre of both lamps in such a way to get irradiated by both lamp equally. The distance between the lamp and outer wall of reactor was 10cm and the experiments were carried in batch mode. These lamps were used as visible light source for lab scale study. For field study instead of visible light source direct sunlight was used.
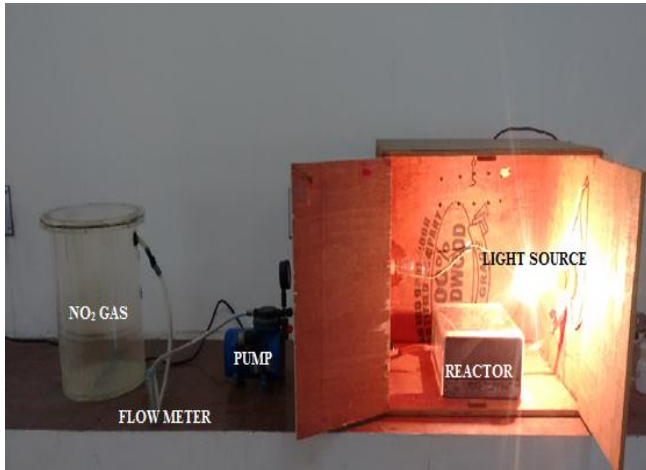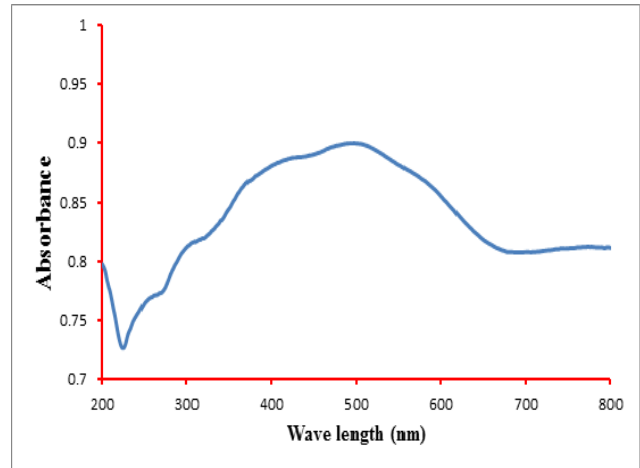
Fig 1. Photographic view of experimental setup

B. Experimental Procedure

Zinc ferrite titania was prepared by sol–gel process and the molar ratio of zinc ferrite to titania is 0.5%. Tetrabutyl titanate, zinc nitrate and ferric nitrate were used as precursors of titania and zinc ferrite, respectively [7]. The prepared catalyst was mixed with few drops of ethanol and coated on the inner sides of vertical concrete block. Within few seconds, ethanol evaporated and catalyst stuck on the surface of cement block. The NO_2 gas was generated in a closed cylindrical vessel by adding copper powder to nitric acid based on the reaction shown in equation 1.

$$Cu(s) + 4HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l) \quad (1)$$
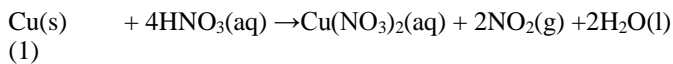
The generated NO_2 gas was supplied to the reactor at a constant flow rate with help of a pump. Two valves were provided on either side of the reactor for controlling the flow of NO_2. After pumping NO_2, two valves were closed and NO_2 was allowed to remain in the reactor where the catalyst was coated for sufficient irradiation time. After known irradiation, NO_2 was pumped from the reactor and absorbed in an absorbing medium consists of sodium hydroxide and sodium arsenite solution. The concentration of NO_2 in the absorbing medium was determined colorimetrically by reacting the nitrite ion with sulfanilamide and N-(1-naphthyl) - ethylenediamine di-hydrochloride (NEDA) at 540 nm and the degradation efficiency was determined based on the initial and final concentrations of NO_2

III. RESULTS AND DISCUSSIONS

A. Characterization of Photocatalyst

The absorption wavelength in the solar spectrum and band gap energy were determined using Ultraviolet Diffusive Reflectance Spectrometry (Make-JASCO, Model name-v-650, Serial number-B089261150). The spectrometry used wavelength in the range of 200-800nm. The absorbance and its wavelength obtained from the UV-DRS analysis for the sample is shown in the Fig 2. The maximum absorbance (0.899823) was observed at a corresponding wavelength of 496 nm, which falls in visible light region of solar spectrum.

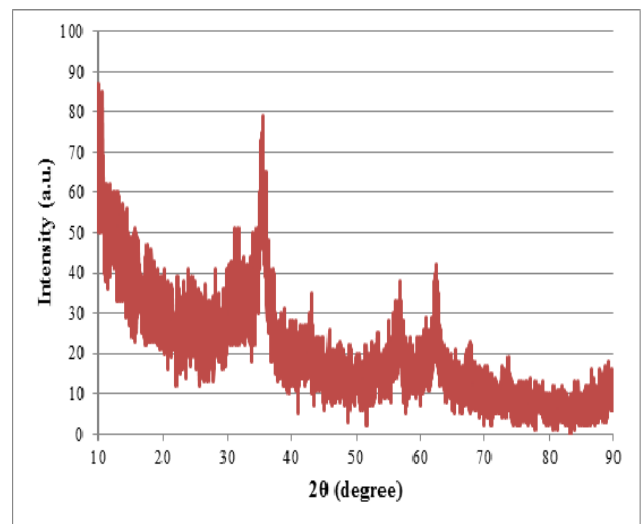Fig 2. Ultraviolet-diffusive reflectance spectra of zinc ferrite titania

Fig 3. X-ray diffraction pattern of zinc ferrite titania

The calculated bandgap energy of zinc ferrite titania was 2.50 eV which is less than that of the commercial TiO_2 (3.2 eV). So it may be understood that zinc ferrite titania would be excited by visible light.

The particle size of the prepared powder was determined using X-Ray Diffraction (XRD) (Make-GE instruction technology, Model No-3003TT) and crystal size of the particle was determined from Scherer equation. X-ray diffraction pattern of the zinc ferrite titania were shown in the Fig 3. The half width full maximum value, 2θ value and the crystal size were found to be (β) 0.157 (radians), 35.5^0 and 9.27nm respectively. The appearance of the peak clearly indicated the nano size of particles. The surface area increases with decrease in size. Thus the prepared catalyst has more surface area which increases the contact area of pollutants with the catalyst when compared to commercial TiO_2.

B. Optimization of Operational Parameters

1) Effect of catalyst dosage on degradation of NO_2

Dosage of zinc ferrite titania was varied both in presence and absence of visible light. The experiment was carried out for an initial concentration of NO_2 of $81.02 \mu g/m^3$ and catalyst dosage varying as 0,2,4,6,8,10 and 12 mg/cm^2 and the removal efficiency are shown in fig 4 .The dark adsorption was carried out in absence of light for the residence time of 24hrs while the experiment with presence of visible light was carried out for a residence time of 30 minutes and in the presence of light having intensity of $8000 w/m^2$. It shows that the dark adsorption of NO_2 increases with increase in catalyst dosage. The increase in adsorption was mainly due to the increase in surface area of catalyst. It was observed that the removal of NO_2 is increasing with increase in catalyst dose in the presence of visible light, however after a dose of 10 mg/cm^2, the increase of dose decreases the removal of NO_2.

On increasing catalyst dosage, more catalyst surfaces will be available for photo oxidation. So the rate of photocatalytic oxidation of pollutants increases due to increasing active sites. But beyond the optimum amount of catalyst loading, the oxidation rate might be reduced as the infiltration depth of the photons is diminished due to screening and shadowing effect of photocatalyst and less photocatalyst could be activated. Therefore, the optimum dosage was found to be 10 mg/cm^2 and the maximum removal efficiency of NO_2 for the initial concentration of $81.02 \mu g/m^3$ was found to be 83.68%. This optimized catalyst dosage is adopted for optimization of other parameters.

Toma et.al (2004) studied photocatalytic degradation of NO_2 using TiO_2. They varied catalyst dosage from 0.01g to 1.2 g and observed that photocatalytic degradation increased proportionally by increasing catalyst dosage and reached a maximum value for 0.2g of the catalyst. Further increase in catalyst dosage results in reduction of degradation rate. Similar behaviors were illustrated by Zhang et al (1994) and Herrmann (1999) who noted that the photocatalytic degradation rate of different aqueous pollutants increased with catalyst mass until a maximum value. The optimum mass corresponds to the case where all TiO_2 particles are irradiated and utilized in the photocatalysis.
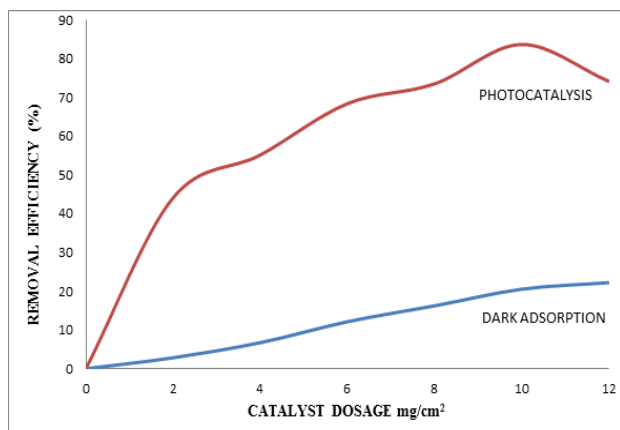
Herrmann (1999) explained that a screening effect occurred when higher powder quantities were used, because the particles that are in excess can mask a part of the photoactive surface. Another factor that can be taken into account is the fact that when the TiO_2 powder bed is important, the photons cannot penetrate and excite all the particles, especially the particles located at the bottom of the powder layer.

2) Optimization of irradiation time

The irradiation time was varied as 5, 10, 15, 20, 25, and 30 minutes for the optimized zinc ferrite titania dosage of $10 mg/cm^2$. The initial and final concentration of NO_2 for different irradiation time was determined. The experiment was carried out for the initial concentration of $81.02 \mu g/m^3$ which was produced in a closed cylinder by the reaction of 0.1g of copper with 0.4 g HNO_3. The experiment was conducted in the presence of visible light of intensity 8000 w/m^2. A plot was made between irradiation time and removal efficiency and it was shown in the Fig 5. From Fig 5 it was observed that catalyst acquire a steady state condition at 20 minutes of irradiation time; further increase of irradiation time would not affect the removal efficiency. The reason for such behavior is the saturation of the active groups on the surface of the catalyst. The optimum irradiation time for the removal of nitrogen dioxide of initial concentration of $81.02 \mu g/m^3$ was found to be 20 minutes. This optimized irradiation time of 20 minutes was adopted for optimization of other parameters

Huang et. al (2010) studied visible light photocatalytic degradation of nitric oxides on PtOx-modified TiO_2 and they reported that the oxidation reaction can only go as far as NO_2 once the catalyst is saturated with NO_3^-. Here catalyst acquired an equilibrium condition after 20 minutes. Bahram et.al (2016) studied Enhanced photocatalytic degradation and mineralization of furfural using $UVC/TiO_2/GAC$ composite in aqueous aolution and reported that Furfural removal increased significantly as UV irradiation time increased but remained almost unchanged after 80 min of irradiation. The removal efficiency of furfural increased with an increase in OH^* generation as more UV light irradiation became available and optimum irradiation time of 80 min was, thus, selected.
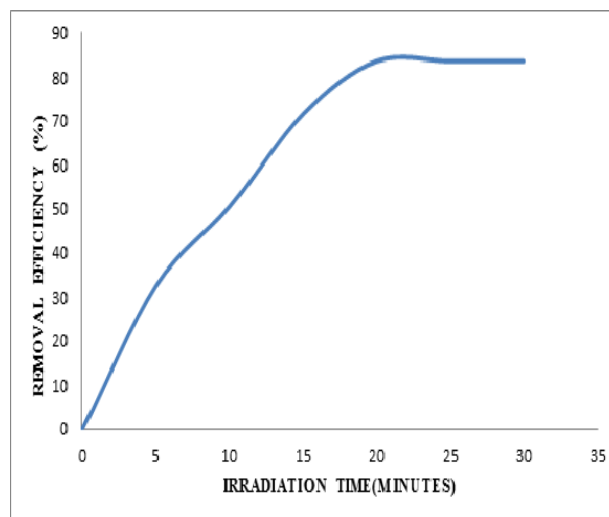

Fig 4. Effect of catalyst dosage on the degradation of NO_2

Fig 5. Effect of light irradiation time on NO_2 degradation

3) Effect of initial concentration of NO_2

Initial concentration of nitrogen dioxide was varied by varying amount of copper and nitric acid. The experiment was conducted with optimized catalyst dosage of $10mg/cm^2$ and optimized irradiation time of 20 minutes. A plot was made between varying initial concentration and removal efficiency and it was shown in the Fig 6.

It was observed that the removal efficiency of nitrogen dioxide is inversely proportional to initial concentration for the optimized dosage and contact time. It might be due to the adsorption of more molecules (NO_2) on the surface of the photocatalyst. This results in unavailability of catalyst surface for the building of hydroxyl radical which reduces the photocatalytic activity of the catalyst. Also, higher initial concentration decreases the number of photons or path length of photon that is arrived on the surface of photocatalyst which reduces the excitation of electron from the valance band to conduction band and as a result the photocatalytic activity decreases. Thus the higher initial concentration requires either more contact time or increased catalyst dosage to achieve maximum removal efficiency.

Bahram et.al (2016) observed in their photocatalytic study that removal efficiency decreased on increasing the initial concentration. This indicates that as the initial concentration increased, molecule adsorption on the surface of the catalyst increased. The high amount of contaminants adsorbed onto the surface of the catalyst inhibited the reaction of contaminant molecules with the photogenerated holes and hydroxyl radicals by preventing direct contact between them. An increase in contaminant concentration caused the molecules to absorb UV rays and the photons never reach the photocatalyst surface; thus, photocatalytic degradation efficiency decreased.

4) Effect of light intensity

The effect of intensity of light was studied by varying intensity of light for optimized catalyst dosage of $10mg/cm^2$ and optimized irradiation time of 20 minutes. Light source used for the experiment consist of two bulbs each of 200W power and having wave length of 465 nm. The intensity of light was varied by switching on one bulb of 200 W and by switching on two bulbs each of 200W. The intensity was calculated by dividing power of bulb by surface area of concrete block where catalyst is coated. The removal efficiency was varied as shown in Fig 7.
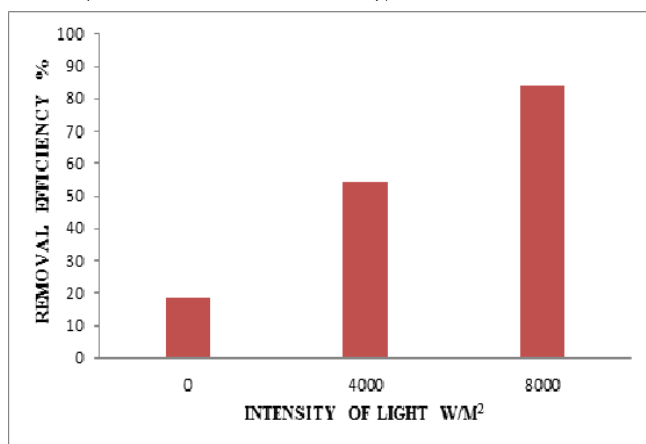
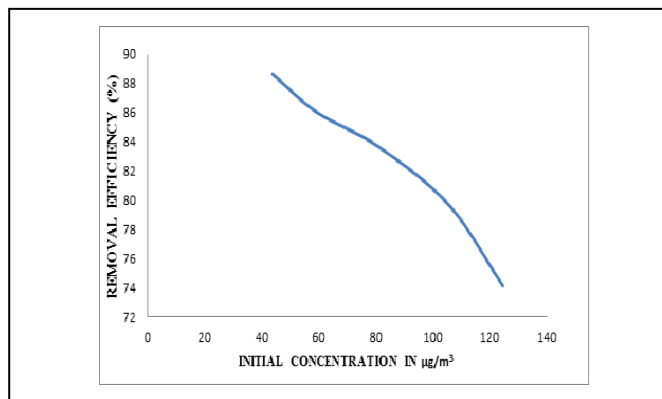Fig 7. Effect of light intensity

Fig 6. Effect of initial concentration of NO_2

It was observed that the rate of reaction linearly increased with light irradiation. Semiconductor catalyst absorbs the light with energy equal to or more than band gap energy which causes the movement of electrons from valence band to conduction band by leaving holes in the valence band and thus the photocatalytic oxidation rate increases with increasing intensity of radiation. At zero intensity of light removal efficiency observed was 18.47. It is due to dark adsorption. Removal efficiency increased by 35.63% when intensity increased to $4000 \ w/m^2$ and 65.21% when increased to $8000 \ w/m^2$.

C. Field Study

For evaluating the performance of the experimental setup under direct sunlight a field study has been conducted. In this study direct sun light had been used instead of artificial visible light source. Nitrogen dioxide degradation efficiency of photocatalyst zinc ferrite titania has been found out at one hour time intervals between 9 am to 5 pm. Two types of field studies were conducted.

Firstly, in order to find out the effect of solar light intensity alone the experiment was conducted with other parameters like initial concentration, catalyst dosage and irradiation time being kept constant. For keeping initial concentration of NO_2 constant, NO_2 was produced synthetically. Experiment was conducted at different time intervals as solar light intensity varies in different time interval. After pumping NO_2 in to the reactor, valves on both sides of reactor were closed and allowed NO_2 to remain in the reactor during irradiation of 20 minutes. After optimum irradiation time of 20 minutes NO_2 was pumped to absorbing solution and final concentration was measured. The removal efficiency was measured for every one hour interval between 9am to 5pm and experiment was conducted as batch process. The initial concentration had taken as $81.02 \mu g/m^3$ and the catalyst dosage used was 10 mg/cm^2. The results obtained are given in Table 1.

From Table 1, it was observed that maximum removal efficiency was obtained in between 1 pm to 2 pm. It might be due to maximum light intensity in this time interval. The maximum efficiency observed was $83.68 \mu g/m^3$ at time interval 1 pm to 2 pm and minimum intensity observed was $74.50 \ \mu g/m^3$ at time interval 4pm to 5 pm and an average efficiency for 8 hour experiment is $80.63 \ \mu g/m^3$. The optimal utilization corresponds to the domain where the destruction rate is proportional to light intensity [8]. The rate of

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photocatalytic degradation increased with increasing light intensity. It might be due to the electron- hole pair generation. Thus more pairs would be available for oxidation and hence, the rate of photocatalytic degradation enhanced.

The photocatalytic degradation of ambient NO_2 by solar light was also studied in the presence of zinc ferrite titania as photocatalyst. The experiment was conducted for a total duration of 8 hours. The reactor was connected to a high volume sampler and kept near traffic intersection (Madhya kylash traffic signal). The setup was operated on hourly basis. The catalyst dosage used was 10 mg/cm^{2}which was the optimum catalyst dosage obtained in lab scale experiment. The initial concentration, final concentration and removal efficiency are described in Table 2.

The setup was operated continuously for 8 hours, in each hour one hour average concentration of NO_2 was measured using personal sampler and it was taken as initial concentration. Concrete block was changed in each hour for coating new catalyst. The variation of initial concentration is mainly due to variation of traffic density. At peak hours the concentration of NO_2 was more due to higher traffic density. At peak hours the concentration of NO_2 was more due to higher traffic density. The variation in removal efficiency of zinc ferrite titania might be due to initial concentration as well as light intensity. As the initial concentration decreases the removal efficiency increased as observed in lab scale study. The maximum removal efficiency observed was 83.68 % at time interval 1 pm to 2 pm and minimum intensity observed was 79.31 % at time interval 9am to 10 am and an average efficiency for 8 hour experiment is 81.23 %.

TABLE 1. EFFECT OF SOLAR LIGHT INTENSITY

Time	Initial concentration ($\mu g/m^3$)	Absorbance	Final concentration ($\mu g/m^3$)	Removal efficiency %
9 am – 10 am	81.02	0.021	17.35	78.58
10 am – 11 am	81.02	0.019	15.69	80.62
11 am – 12 pm	81.02	0.018	14.87	81.64
12 pm – 1 pm	81.02	0.017	14.04	82.66
1 pm – 2 pm	81.02	0.016	13.22	83.68
2 pm – 3 pm	81.02	0.017	14.04	82.66
3 pm – 4 pm	81.02	0.019	15.69	80.72
4 pm – 5 pm	81.02	0.025	20.58	74.50
average				80.63

TABLE 2. PHOTODEGRADATION OF AMBIENT NO_2

Time	Initial concentration ($\mu g/m^3$)	Final concentration ($\mu g/m^3$)	Removal efficiency %
9 am – 10 am	63.59	13.15	79.31
10 am – 11 am	61.82	12.29	80.11
11 am – 12 pm	42.36	7.88	81.39
12 pm – 1 pm	28.14	4.95	82.40
1 pm – 2 pm	23.21	3.78	83.68
2 pm – 3 pm	21.23	3.62	82.94
3 pm – 4 pm	24.34	4.83	80.14
4 pm – 5 pm	34.68	6.97	79.91
average	37.42	7.18	81.23

The removal efficiency of zinc ferrite titania obtained in lab scale study was 83.68% and it was around 81.23 % in the field, i.e. The removal efficiency obtained in field study was slightly lesser than that of lab scale study. It may be due to the variation of light intensity, initial concentration and interference of other pollutants. The removal efficiency of Ni doped TiO_2 was33% (Tseng et.al 2010) and Pt doped TiO_2 was 45% for initial concentration of 1 ppm in the lab scale study at room temperature (Huang et.al 2010). The cost platinum is more when compared to zinc ferrite .TiO_2 and Ni doped TiO_2 was active only at UV light which accounts for 3 to 4 percentage of sunlight. Thus zinc ferrite titania is better when compared to other catalysts.

IV.   CONCLUSION

The photo catalytic experiment for the degradation of NO_2 indicates that zinc ferrite titania can effectively catalyse photodegradation of NO_2 in visible light irradiation. The maximum removal efficiency in lab scale experiment for an initial concentration of 81.02 $\mu g/m^3$ obtained was 83.68% with optimized catalyst dosage of 10 mg/cm^2 and optimized irradiation time of 20 minutes. An average removal efficiency of 81.23 % was observed in field level study using ambient air as NO_2 source and solar light as light source.

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