

Development and Demonstration of Nano-sized TiO₂ – based Photocatalytic Oxidation Technology for Controlling VOCs

(Outcomes of the Project for Beneficiaries and Field Applications)

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Introduction

Volatile organic compounds (VOCs) of anthropogenic origin are important air pollutants emitted largely by industries, vehicles and domestic cooking using fossil fuels, especially bio-fuels. Many VOCs (e.g., benzene, toluene, ethylbenzene and xylene (BTEX)) are toxic and some are carcinogenic, mutagenic or teratogenic. The recent research efforts for removal of VOCs have focused on advanced oxidation processes such as photo catalytic oxidation (PCO) in presence of semiconductor photocatalyst. In PCO, formation of hydroxyl radical in presence of water vapour is primarily responsible for converting organic compounds into simple products such as water vapour and carbon dioxide. The titanium-di-oxide (TiO₂) based PCO of VOCs has high potential for cleaning industrial emissions and indoor air. However, the field application of PCO related technology for VOC control remains a challenge due to many issues that need to be addressed. The challenges include particle size of TiO₂, effective coating, activation and deactivation of catalyst surface, uncertainties in estimated degradation rate constant and long-term application of PCO technology. Further, the complete oxidation of VOCs does not happen instantly. Some intermediates will be formed due to partial oxidation and may be harmful to the building occupants.

To address the above issues, this project has focused on: (i) laboratory study for improving PCO technology (ii) field applications of technology and (iii) characterizing the risk of exposure to intermediates and suggesting degradation pathways of BTEX. Based on the analyses and interpretations of results, and pilot testing in the field, the technology is ready for wider acceptance and field applications.

Technology Development

Preparation of TiO₂ Coating

All chemicals that are used should be of analytical reagent (AR) grade. Sol-gel process comprising hydrolysis, condensation and formation of thin TiO₂ film at low temperature was used for coating TiO₂ inside the reactor surface (quartz or aluminium). This method provided the best coating results for surface morphology, particle size, film thickness, band gap energy etc. Two sols (Sol A and Sol B) were prepared from a mixture of titanium tetra-iso-propoxide (TTIP; 98%; Spectrochem, Mumbai), di-ethanolamine (DEA; 99.5%; Merck, Mumbai), acetyl acetone (AcAc; 99.55%; Loba Chemicals), de-ionized water (H₂O) and ethanol (C₂H₅OH) at a molar ratio of 1:1:0:0:34 (Sol A) and 1:0:1:3:20 (Sol B) respectively. Sols A and B were mixed and ultrasonicated for 30 minutes to get the final sol-gel. For coating, the following procedure was followed; filling of the reactor with the sol-gel, emptying it gradually after 2-3 minutes, drying slowly at room temperature for 10 minutes, heating in a hot air oven at 120 °C for 10 minutes, transferring into a muffle furnace at 500 °C for 15 minutes followed by cooling at room temperature for 10 minutes. The entire process was repeated 15 times to obtain the optimal catalyst film of TiO₂.

Kinetic of VOCs Degradation in Batch Reactor

The TiO₂ coated reactor was used to study the kinetics of the PCO of individual VOCs with the UV lamps of 8, 11 and 16 Watts in a batch process. The degradation rate for VOCs for different UV lamp

wattage followed first order kinetics. The values of degradation rate constants (k) for the above three wattage for an operation period of 120 min are shown in Table 1. Rate constant increase with wattage of the UV lamp and is maximum for benzene. The estimated k values can be used to design a continuous reactor system for removal of VOCs at a desired efficiency. The degradation rates determined in this study are: 0.089 min^{-1} (i.e. $1.69 \text{ min}^{-1}\text{m}^{-2}$ for 16W UV) for toluene and 0.094 min^{-1} (i.e. $1.79 \text{ min}^{-1}\text{m}^{-2}$) for benzene.

Table 1: Degradation rate Constants (k) for VOCs in $\text{min}^{-1}\text{m}^{-2}$ of TiO_2 surface area

| Compound | Initial concentration (mg/m^3) | Degradation rate constants (k) ($\text{min}^{-1}\text{m}^{-2}$) | | |
|-------------|--|---|-----------------|-----------------|
| | | 8W UV lamp | 11W UV lamp | 16W UV lamp |
| Benzene | 150 ± 30 | 1.65 ± 0.08 | 1.63 ± 0.03 | 1.79 ± 0.05 |
| Toluene | 161 ± 26 | 1.44 ± 0.05 | 1.49 ± 0.06 | 1.69 ± 0.07 |
| ETB | 170 ± 21 | 1.21 ± 0.04 | - | - |
| p, m-Xylene | 181 ± 25 | 1.26 ± 0.07 | 1.35 ± 0.08 | 1.45 ± 0.03 |
| o-Xylene | 120 ± 27 | 1.14 ± 0.03 | - | - |

Proto Type Device

A proto type device (Figure 1) consisting of seven numbers of reactors in series was fabricated and installed in three indoor environments to examine field worthiness of technology. Through the help of flow regulator and rotameter, the flow rate of VOC laden stream (into the device) was set to desired level. The Total Volatile Organic compounds (TVOC) concentration was measured through a TVOC analyzer (ppb RAE 3000, Honeywell, CA 95134-1708 USA) at the inlet and outlet of the device.

Degradation rate as function of duration of reactor operation

One reactor for each VOC was operated successively (without regeneration) for 0-1, 1-3, 3-5, 5-7, 7-9, 9-11, 11-13.5 hours, and the degradation rate was examined (Figure 2; as an example of benzene). It is important to note that in each successive experiments, the degradation rate constant for each compound progressively decreased, due to deactivation of catalytic surface with time (Table 2). This is possibly due the formation of highly adsorbed intermediates during the PCO of VOCs that leads to an abrupt decrease in the number of active sites during the reaction on catalyst surface.



Figure 1: Full-scale VOC control device (schematic)

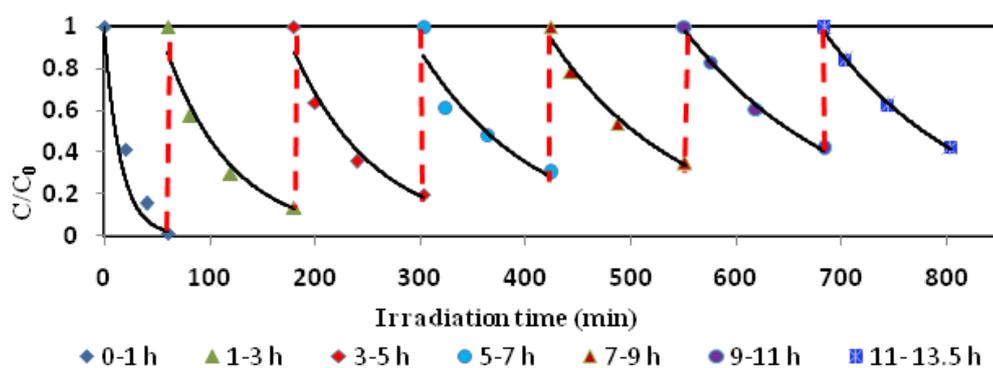


Figure 2: Variation in degradation kinetics over time for PCO of benzene in 8W UV lamp

Table 2: Degradation rate constants (k) of VOCs in $\text{min}^{-1}\text{m}^{-2}$ of TiO_2 surface area

| Reactor operation time(hr) | Degradation rate constant(k ; $\text{min}^{-1}\text{m}^{-2}$) | | | | | | | |
|----------------------------|---|----------------|---|----------------|--|----------------|---|--|
| | Benzene ($C_i=211\pm 21\text{ mg/m}^3$) | | Toluene ($C_i=162\pm 18\text{ mg/m}^3$) | | p,m-Xylene ($C_i=153\pm 14\text{ mg/m}^3$) | | Ethyl benzene ($C_i=177\pm 19\text{ mg/m}^3$) | o-xylene ($C_i=143\pm 16\text{ mg/m}^3$) |
| | 8W UV | 16W UV | 8W UV | 16W UV | 8W UV | 16W UV | 8W UV | 8W UV |
| 1 | 1.7 ± 0.09 | 1.79 ± 0.05 | 1.49 ± 0.06 | 1.69 ± 0.07 | 1.32 ± 0.03 | 1.45 ± 0.04 | 1.24 ± 0.02 | 1.16 ± 0.06 |
| 3 | 1.50 ± 0.04 | 1.74 ± 0.06 | 1.39 ± 0.22 | 1.65 ± 0.04 | 1.22 ± 0.14 | 1.4 ± 0.05 | 1.17 ± 0.13 | 1.12 ± 0.03 |
| 5 | 1.31 ± 0.15 | 1.71 ± 0.03 | 0.93 ± 0.31 | 1.39 ± 0.02 | 0.93 ± 0.11 | 1.05 ± 0.06 | 0.86 ± 0.09 | 0.81 ± 0.12 |
| 7 | 0.88 ± 0.07 | 1.66 ± 0.07 | 0.82 ± 0.25 | 1.03 ± 0.08 | 0.81 ± 0.08 | 0.84 ± 0.04 | 0.78 ± 0.04 | 0.76 ± 0.05 |
| 9 | 0.74 ± 0.09 | - | 0.71 ± 0.09 | - | 0.7 ± 0.12 | - | 0.68 ± 0.07 | 0.66 ± 0.08 |
| 11 | 0.69 ± 0.03 | - | 0.63 ± 0.05 | - | 0.62 ± 0.03 | - | 0.61 ± 0.07 | 0.57 ± 0.04 |
| 13.5 | 0.65 ± 0.05 | - | 0.60 ± 0.06 | - | 0.59 ± 0.02 | - | 0.56 ± 0.05 | 0.56 ± 0.03 |

C_i : Initial VOC concentrations

Regeneration of Catalyst

Three different techniques were employed to regenerate the catalyst to remove/oxidize the deposited organics to CO_2 and water. These techniques are (i) heating of reactor at $450\text{ }^\circ\text{C}$ for 15 minutes (ii) irradiation of surface with 16W UV lamp and (iii) washing of surface with a strong oxidizing agent H_2O_2 . Heating regenerates the catalyst fully as all organics (parent compound and intermediates) were evaporated and/or oxidized at $450\text{ }^\circ\text{C}$ and surface was regenerated to its original value and regeneration through heating is strongly recommended.

Based on characterization of catalyst surface for structural continuity, surface roughness, surface impurities, strong surface attachment and particle size, a standardized sol gel coating method was established to apply TiO_2 on borosilicate glass substrate. The particle size of coated TiO_2 was in nano size ($10.2\pm 1.43\text{ nm}$) that should ensure large active surface area (around $100\text{ m}^2/\text{g}$) of catalyst. This study has estimated the degradation rate of BTEX for ultra violet (UV) lamps of 8W, 11W and 16W. The highest degradation rate was obtained for 16W UV lamp. The high wattage of lamp results in increased running cost but there is an opportunity to optimize the process based on increased wattage versus increased efficiency.

Field Application and Pilot Testing

After addressing the impending challenges, the technology was taken to field after scaling up the laboratory reactor to pilot plant. The effectiveness of technology for different VOCs (benzene, chlorobenzenes (mono, di and tri) and mixture of solvents present in chemistry laboratory) was established. It was noted that the estimated degradation rate constant for coexisting multiple VOCs was $1.06 \text{ min}^{-1} \text{ m}^{-2}$ (surface area of catalyst), which in comparison to that of benzene ($1.6 \text{ min}^{-1} \text{ m}^{-2}$), is smaller by 34 percent because of concurrent competitive reactions on the surface of catalyst. The control efficiency of device was over 99 percent for benzene, 88 percent for multiple VOCs and 71 percent for chlorobenzenes.

The major focus of the project was to pilot test the technology in the field and addresses all the issues of technology up-gradation. Specifically new equipment was designed based on the degradation rates estimated from laboratory studies (carried out in this project) reduction in the efficacy of catalyst with its use. The impediment and difficulties encountered in earlier versions have been taken in consideration while designing the new units which is easy to operate and cost effective as pressure drop has been reduced significantly. The technology is at a stage where it can be adopted by the industry (see Figure 3 for field performance).

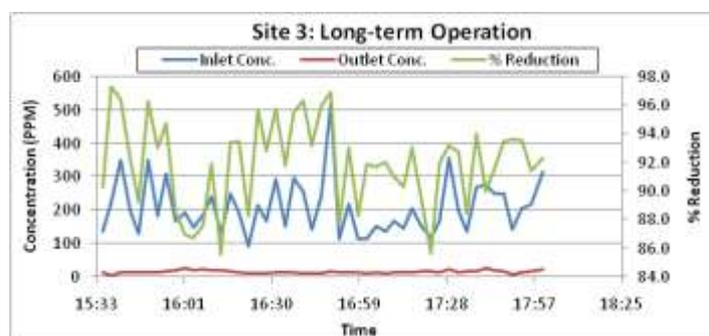


Figure 3: Long-term VOC Emission and Control at Site-3

Scaled-up Control Equipment

The new equipment was designed based on the degradation rates estimated from laboratory studies (carried out in this project) reduction in the efficacy of catalyst with its use. The impediment and difficulties encountered in earlier versions have been taken in consideration while designing the new units. The specific features of the new equipment (Figure 4) are given below. The pictures inside and outside of the devices are given below.

- The device can handle about 90 litres per minute (LPM) of polluted air compared to earlier system handling 6-10 LPM of air
- The device is made of aluminium which is light in weight which is easy transport
- The coating substrate is aluminium plates and not glass which was fragile and could break
- The system uses both sides of the plates for catalyst coating and thus will have improved VOC reduction
- The coated plates are of front loading and thus has an ease of operation (while inserting or taking out the plates)

- All the connections through narrow tubes and holes have been avoided and thus pressure drop is minimized.
- The temperature and humidity meters have been installed for better control of process
- The overall dimension is 140 cm× 35 cm× 30 cm with eight number of plates (30 cm × 20 cm)
- There are total 24 UV lights of 16 W each capacity
- The system is completely enclosed to avoid the exposure to the UV light
- Special feature is the design of see through glass window for assessing operation of the system.
- An air tight and leak-proof system.

The new equipment was tested and it showed an average reduction of about 75% in benzene.



Figure 4: Images of the Scaled-up VOC Control System