CHAPTER V

CONCLUSIONS

In the present research work, synthesis of potential photocatalytic nanomaterials was carried out under sol-gel and hydrothermal technique using different precursors. As-prepared photocatalytic nanomaterials were characterized by various analytical techniques to study on obtained functionalities under varied experimental conditions. Photocatalytic degradation of selected volatile organic compounds (VOCs), which generally emitted by industrial activities into environment was carried out under various experimental conditions and light sources. Titanium dioxide (TiO$_2$) and zinc oxide (ZnO) semiconductors with band-gap of 3.22 and 3.37 eV respectively were selected as the core photocatalyst for degradation of VOCs. Semiconductor based photocatalysts were prepared in the form of nanomaterials as they are more effective as nanoparticles when compared to the bulk photocatalyst. The activation of pure TiO$_2$ and ZnO takes place under UV light radiation and generally unstable in state. The wide band-gap energy of both TiO$_2$ and ZnO was reduced by the doping suitable metal/non-metal ions or by modifying the addition of co-catalysts, so as to reduce the band-gap energy and also reduce the recombination rate of electron-hole pair.

Nitrogen (N) doped TiO$_2$ was synthesized by sol-gel method using titanium isopropoxide, ethyl alcohol as precursors. The prepared photocatalytic nanomaterials were coated on to the surface of calcium aluminium silicate beads using the binding agent. N doped TiO$_2$ has a band-gap energy of 3.2 eV at a wavelength of 390 nm and 3.12 eV at a wavelength of 405 nm, clearly indicating a reduction in the band gap energy at the visible range spectrum. Particle size of 34.5 nm was obtained for N doped TiO$_2$, which was determined using X-ray diffraction results and applying Scherrer formula. FTIR results of N doped TiO$_2$ displayed the stretching band which corresponds to the nitrogen in the lattice structure, observed at lower energy absorption region in the FTIR spectrum. Photocatalytic degradation of methylene blue using N doped TiO$_2$ nanomaterial was studied for varying operating conditions such as light source (Tungsten, LED, UV light), photocatalyst load, reactor configuration (batch, packed and fluidised bed reactor) and also reusability of the photocatalyst. In a batch reactor, 400 mg/L of photocatalyst load degraded the methyl benzene concentration from 270 μg to 140 μg with an efficiency of 48 %. For a packed bed reactor 40 % of degradation was achieved for duration of 5 h. Further research needs to be done regarding the effect of experimental duration after 5 h in the degradation of the methylbenzene in a continuous packed bed reactor. Fluidised bed reactor was more efficient in the degradation of methyl benzene to 74% within duration of 5 h; whereas 40% and 50% was achieved with packed bed and batch studies respectively. Recovery and reuse of the photocatalyst also revealed that the photocatalyst can be reused 4–5 times. Coated ceramic beads indicated that photocatalytic degradation is taking place only due to the presence of photocatalyst.

A nanocomposite of TiO$_2$ was prepared using soft-chemical method using titanium dioxide, manganese sulphide, cerium oxide and ferrous oxide as precursors. As-obtained Fe-Mn-CeO$_2$/TiO$_2$ nano-composite was further characterized and photocatalytic degradation studies were carried out. The band-gap energy of the prepared nano composite was considerably shifted toward visible spectrum (3.17 eV and 2.96 eV) that indicates the utilization nano-composite for degradation of VOCs under natural sunlight as an alternative driving energy. Other characterizations were also confirmed well crystalline structure, structural elucidation, nano-scale poly crystalline phase and potential photocatalytic activities that apparently enhance the
photocatalytic degradation rate of VOCs. Photocatalytic activity of nanocomposite for the degradation of bromobenzene was studied for different parameters viz., light source (sunlight, tungsten, UV and LED), photocatalyst load, and initial concentration of bromobenzene, pH, and irradiation time. The photocatalytic study of bromobenzene revealed that the optimum photocatalyst concentration is 20mg/L; with initial concentration of the bromobenzene 300mg; with the optimum pH of 4 along with an LED light source and for a duration of 20 hours 98 % of degradation efficiency was obtained in a batch reactor.

Modified TiO$_2$ nanomaterial was prepared under hydrothermal method using titanium P25 as the precursors and 10M NaOH. During hydrothermal preparation of modified TiO$_2$, Central Composite Design (CCD) a statistical tool was used to arrange the hydrothermal settings for aging temperature (120 – 180°C) and time (8 – 24 hrs). The obtained results under CCD analysis clearly confirmed desired properties under fixed optimized conditions and it was well correlated with experimental conditions from the perspective of characterization and degradation of paraquat in aqueous media. The modified photocatalyst was used for the photocatalytic degradation of paraquat, a pesticide. Crystalline size, photocatalytic degradation and adsorption studies were used as the response for the CCD and aging temperature and time were considered as the dependent variables. Band-gap energy of the modified TiO$_2$ was in the range of 2.65 to 2.94. The XRD patterns of all the samples are found to be in the anatase crystalline phase except for 195°C/16 h. The crystallite growth of titania nanotubes was increased from 105°C to 150°C with increasing in the intensities of anatase peaks. SEM analysis revealed TiO$_2$ tubular structure for 195°C/16 hrs sample and increase in duration of reaction at 150°C resulted in shape transformation. Particles with round morphology were observed uniformly for the 105°C/16 h samples. The significant effect on percent removal of paraquat by photocatalytic degradation and by adsorption was aging temperature and its square term, while the aging time was insignificant for both the responses. For percent removal by adsorption, the interaction becomes significant, whereas for photocatalytic degradation, the interaction was insignificant. The error of this model was also insignificant for all the three responses. The optimum condition for percent paraquat removal by adsorption was 150°C at 4 hrs and for photocatalytic degradation was 105°C at 16 hrs.

ZnO nanoparticles were prepared by using sol gel technique under alkaline conditions. Doping was carried out for ZnO using silver, cadmium and lead. For the synthesis of Cd and Pb, zinc sulphate heptahydrates was used as precursors and for Ag doping zinc nitrite was used as precursors. The band-gap energy for Ag/ZnO, Cd/ZnO and pb/ZnO are 2.97, 2.91 and 2.81 eV respectively. XRD pattern of modified ZnO revealed highly crystalline phase and the average crystalline sizes were 191.8, 287.7 and 71.9nm. SEM analysis of Ag/ZnO and Cd/ZnO were observed to be poly-scale in nature and agglomerated where Pb/ZnO nanoparticles appeared in the form of nano-rods of approximately 60 to 150nm range. FTIR spectrum of Ag/ZnO and Cd/ZnO nanoparticles showed broad stretching vibration bands at 900-1150 cm$^{-1}$ corresponding to Zn-O-Ag and Cd-O-Zn respectively that indicates the interfacial region of ZnO and dopants. FTIR spectrum of Pb/ZnO nanoparticles showed narrow stretching vibration bands at 900-1150 cm$^{-1}$ corresponding to Pb-O-Zn and intensity of stretching bands corresponding to Pb-O-Zn comparatively high that indicates the presence high Pb in ZnO crystalline structure. The average sizes of Ag/ZnO, Cd/ZnO and Pb/ZnO nanoparticles were observed in the range of 210-350 nm, 150-360 nm and 60-165 nm respectively as observed by DLS. Pb/ZnO nanoparticle showed increased BET surface area of 106.65 m$^2$/g as compared to Ag/ZnO and Cd/ZnO of 7.75 and 10.6 m$^2$/g. Photocatalytic degradation of methylene blue under the different light source showed good removal efficiency for LED light source
and for Pb/ZnO when compared with Ag/ZnO and Cd/ZnO. Photocatalytic degradation of chlorobenzene was experimented in a batch scale reactor under different light source. 96, 91 and 100% efficiency was obtained under LED light source for Ag/ZnO, Cd/ZnO and Pb/ZnO respectively. A Pb/ZnO nano particle was found to be effective with rapid degradation rate of chlorobenzene under light source within a short duration of 1 hour. A lab scale continuous photoreactor model was designed and demonstrated for the degradation of VOCs such as methylbenzene and chlorobenzene at laboratory scale. The results clearly showed potential degradation of VOCs up to 99% using continuous photoreactor set-up within short duration under LED light source. In immobilized type, Pb/ZnO nanoparticles were coated inner surface of outer shield by spreading technique using water proof binding agent. Slurry type of photocatalytic degradation processes showed highest degradation efficiency when compared to floating and immobilized type of catalyst load.

Based on the results obtained in the present research work, the following conclusions are made:

- Hydrothermal and sol-gel techniques are the potential methods for the preparation of efficient photocatalytic materials.
- Photocatalytic materials prepared under hydrothermally and sol-gel techniques showed desired functionalities that apparently shows potential photo-degradation efficiency due well crystalline structure and surface area.
- Both modified TiO$_2$ and ZnO nanomaterials showed highest degradation efficiency under visible light sources and these nanomaterials would be used as potential photocatalysts for degradation of toxic organic pollutants including VOCs in environment using natural sunlight as an alternative driving energy.
- Laboratory scale photoreactor designed during the study confirmed considerable level of VOCs degradation under LED light and that can be up-scaled for real time applications at industrial level.
- Photocatalyst assisted photo-degradation of toxic VOCs in environment would be alternative treatment method that is eco-friendly, economic and effective when compared to conventional methods.