# Summary and Conclusions

The study and development of efficient $TiO_2$ combinate photocatalysts for treatment and safe disposal of pollutants in an environmentally acceptable manner at a reasonable cost using solar energy is the main aim of the thesis. In this regard, attempts are made to hybridize adsorption and photocatalysis techniques for the degradation of pesticides in wastewater. The efforts put forward for developing a technology in the present thesis is very much cost effective, safer and environmentally significant in comparison to the available conventional methods. The summary of results obtained in the present investigation is listed below.

## Chapter 3

- $TiO_2$/HY prepared by SSD show the intensified $TiO_2$ anatase phase at 10 wt% $TiO_2$ loading compared to impregnated one. This is due to $TiO_2$ particles residing in the zeolite cavities or channels and may interact with the zeolite frame work in the impregnated catalyst. The broad band peak at 908 $cm^{-1}$ in FT-IR confirms the Ti species occurrence in the zeolite cavities in the impregnated catalyst, which is not present in SSD prepared sample.
- The $TiO_2$/HY zeolite characterization (XRD, SA, SEM-EDAX, TEM and UV-Vis DRS) techniques reveal the well dispersion of $TiO_2$ on the surface of zeolite in the SSD method of preparation.
- By increasing $TiO_2$ loading, the adsorption capacity of zeolite decreased due to high dispersion of $TiO_2$ on the zeolite surface.
- The amount of $TiO_2$ loading is optimized at 10 wt% $TiO_2$/HY (SSD) and it shows high photoactivity for isoproturon degradation, which is more efficient compared to brae $TiO_2$. This is due to the synergistic effect resulting from the adsorption properties of HY that pools the pollutant molecules which are easily accessed by

the $TiO_2$. Furthermore, the zeolite frame work delocalizes or delay the $e^-/h^+$ recombination process for enhanced activity.

- ✍ Adsorption capacity of the combinate zeolite system in impregnated sample is affected negatively compared to SSD. Also SSD method is more photoactive than impregnated combinate because of uninteracted form of $TiO_2$ presence in SSD whereas in impregnation it is present in cavities and also interacted with frame work of zeolite.
- ✍ The catalyst amount 1 g $L^{-1}$ and neutral pH are found to be the optimum parameters for better degradation of isoproturon.
- ✍ The reaction is fallowing pseudo first order rate reaction and 5.98 x $10^{-6}$ M $L^{-1}$ $min^{-1}$ degradation rate is observed at 1.14 x $10^{-4}$ M isoproturon.
- ✍ The catalyst activity is sustainable as evidenced by SEM and UV-Vis DRS techniques even after 3$^{rd}$ cycle of usage.
- ✍ Technical grade pirimicarb is efficiently degraded by the combinate within 150 min and also the commercial grade imidacloprid and phosphamidon are degraded to 90% within 300 min showing faster activity compared to bare $TiO_2$ sample.

In conclusion, the study highlights an easy, simple preparation and efficient use of $TiO_2$/HY combinate catalysts for the photocatalytic degradation of pesticides compared to bare $TiO_2$.

## Chapter 4

- ✍ 1, 5, 10, 15 and 20 wt% preformed $TiO_2$ are dispersed over H-MOR zeolite using solid state dispersion (SSD) method. All these catalysts are characterized by XRD, FT-IR, SEM and UV-Vis DRS techniques and they revealed well dispersion of $TiO_2$ on the surface of zeolite.

- By increasing $TiO_2$ loading, adsorption capacity of the zeolite is decreased due to high dispersion of $TiO_2$ on the zeolite surface.
- The zeolite-supported 15 wt% $TiO_2$ composite is proven to exhibit high efficiency for photocatalytic degradation of isoproturon. Also, high $TiO_2$ loading is found to be detrimental for the photodegradation due to poor adsorption and it distracts from utilization of holes and OH radicals effectively.
- The catalyst amount 1.5 g $L^{-1}$, pH 7 and $1.14x10^{-4}$ M isoproturon concentration are found to be the optimum parameters for higher degradation rates.
- The reaction is found to follow L-H model and proving that degradation is occurring at the solid-liquid interface and fits into pseudo first order kinetics.
- The catalyst activity is sustainable even after $4^{th}$ cycle as is evidenced by XRD, SEM and UV-Vis DRS techniques.
- Pirimicarb is degraded efficiently within 90 min over 15 wt% $TiO_2$/H-MOR compared to $TiO_2$. Also the commercial formulations of imidacloprid and phosphamidon are degraded completely in 240 and 90 min respectively.

The study highlights an easy, simple preparation and efficient use of $TiO_2$/H-MOR for the treatment of pesticide containing wastewater using solar light.

## Chapter 5

- The unique pore properties, high surface areas and facile pore diffusion of bulky substrates paved their way to emphasize the growth of mesoporous molecular sieve science for photocatalytic applications. In this regard, $TiO_2$ is immobilized on mesoporous material like Al-MCM-41 to achieve a novel mesoporous combinate photocatalyst for the treatment of pesticide containing waters.

- The $TiO_2$ wt% 3, 5, 7.5, 10 and 15 supported over Al-MCM-41 by SSD method and equivalent to 10 wt% $TiO_2$ also is incorporated in the frame work of Al-MCM-41 directly during the preparation (isomorphous substitution).
- Intensity of the titania peak in the XRD patterns are reduced for Ti-Al-MCM-41 isomorphous substitution method of preparation compared to SSD method. The FT-IR study is showing the Ti-O-Si linkage in Ti-Al-MCM-41 and also is clearly evidenced by XPS, the same is not present in SSD method of preparation.
- Ti-Al-MCM-41 catalyst adsorption capacity and photocatalytic activity are negatively affected compared to $TiO_2$/Al-MCM-41 (SSD). This is due to the interaction of Ti with Si and Al in the frame work, which is resulting less number of active sites available for photo reaction. In SSD, more active sites are present on the surface and readily available for photocatalytic reaction.
- The 10 wt% $TiO_2$ loading, catalyst amount 1 g $L^{-1}$ and neutral pH are found to be the optimum parameters for an easy degradation of isoproturon.
- The catalyst activity is sustainable even after $4^{th}$ cycle and is evidenced by SEM and UV-Vis DRS.
- The TOC data provides the rate of mineralization of isoproturon is faster upto 80% and later found to slow down due to the formation of aliphatic compounds formation during the degradation path way.
- The complete degradation of pirimicarb is within 45 min over titania supported over Al-MCM-41 combinate and ~5% is remaining over $TiO_2$ even after 240 min of irradiation.
- The commercial formulations of imidacloprid and phosphamidon are successfully degraded over supported catalyst within 300 min and 120 min respectively.

The adsorption and electron delocalization properties of Al-MCM-41 are the key factors for enhancing degradation of pesticides under investigation. Hence, $TiO_2$/Al-MCM-41 composite system is an effective and promising photocatalyst for the abatement of pesticides in contaminated waters.

## Chapter 6

- The investigation illustrates preparation of novel porous nanosilica (PNS) system and its role as support for immobilization of $TiO_2$.
- The morphology of PNS has hexagonal array with a wide distribution of pores with low surface area and is very amorphous in nature.
- $TiO_2$ 1, 5 and 10 wt% is supported over the novel support by SSD method. The fine distribution of titania over the support is evidenced by XRD, SEM and TEM.
- Increasing $TiO_2$ loading the adsorption capacity of the support reduced. The photocatalytic activity results conclude that 5 wt% $TiO_2$ supported on PNS is an efficient catalyst for the degradation of pesticides.
- The catalyst amount 3 g $L^{-1}$, substrate concentration 1.14x $10^{-4}$ M and neutral pH are found to be the optimum parameters for the higher isoproturon degradation rates.
- The TOC data illustrates the rate of mineralization of isoproturon is faster upto 77% within 3h, later it is slow. This may be due to the aliphatic intermediate compounds formation during the degradation path.
- The catalyst activity is sustainable even after $4^{th}$ cycle (as evidenced by XRD, SEM and UV-Vis DRS techniques).
- The commercial pesticide solutions containing imidacloprid and phosphamidon are also proved to be successfully and efficiently degraded by 5 wt% $TiO_2$/PNS

combinate. The complete degradation of pirimicarb occurs in 60 min compared with $TiO_2$ only 60% degradation is observed.

It is proved that 5 wt% $TiO_2$/PNS catalyst is found to be efficient to degrade the pesticides in water.

## Chapter 7

- SBA-15 is synthesized successfully and 1, 5, 10 and 15 wt% $TiO_2$ is loaded over the same by SSD method. $TiO_2$ is dispersed well over SBA-15 without affecting its photocatalytic activity. The well dispersion of titania is evidenced by XRD, UV-Vis DRS, SEM and TEM.
- The 10 wt% $TiO_2$ loading over SBA-15, catalyst amount 1.0 g $L^{-1}$ and neutral pH are the optimum conditions for obtaining higher degradation rates.
- The catalyst activity is sustainable even after $4^{th}$ cycle (as evidenced by XRD, SEM and UV-Vis DRS techniques).
- The TOC data provides the rate of mineralization of isoproturon is faster up to 85% (4h) and later found to be slow. The total disappearance of isoproturon takes within 30 min and ~0.3 mg $L^{-1}$ TOC is remained at the $9^{th}$ hour of the reaction is due to the formation of aliphatic compounds during the degradation pathway.
- The complete photocatalytic degradation for pirimicarb 45 min, for commercial formulations of imidacloprid 180 min and phosphamidon 60 min are observed over 10 wt% $TiO_2$/SBA-15. In all cases the supported catalyst is highly efficient compared to bare $TiO_2$.
- Pesticide consortium with 20 ppm of technical isoproturon and each 15 ppm of imidacloprid and phosphamidon commercial formulations (total 50 ppm) are successfully and very efficiently degraded over 10 wt% $TiO_2$/SBA-15 with the established conditions.

Thus, it is proved well that 10 wt% $TiO_2$/SBA-15 combinate is found to be a very efficient system to degrade the pesticides containing water using solar light.

## Conclusions

- ☞ In order to avoid the post treatment filtration process (simple decantation) efforts were successful in developing an easy and efficient $TiO_2$ combinate photocatalysts for effective photocatalytic treatment of pesticides containing waters.
- ☞ The preparation of supported combinate materials by SSD method is found to be efficient compared to impregnation and isomorphous substitution. This is due to Ti-O-Si linkage formation with the support in the impregnation and isomorphous substitution methods.
- ☞ The more siliceous support system is found to be more active for the degradation of pesticides compared to high Si/Al support systems. This may be the electron delocalization capacity of the framework and synergistic effect between the adsorption capacity and surface area of the catalyst.
- ☞ The pesticide adsorption capacity of the support depends on the Si/Al ratio, frame work type and surface area of the support. The order of adsorption capacity is Al-MCM-41= H-MOR> HY> PNS≥ SBA-15.
- ☞ The attempt for novel preparation of PNS using styrene acrylic acid emulsion and $TiO_2$/PNS combinate photocatalyst systems are successful for making pesticide degradation photocatalysts, which proved to be one of the best reported systems.
- ☞ The 10 wt% $TiO_2$/SBA-15 photocatalyst has emerged as the best photocatalyst for the degradation of pesticide in water solutions due to its high surface area and electron delocalization capacity.
- ☞ All the degradation reactions are following the pseudo first order kinetics. It can be concluded that pH 7, surface area of 430 $m^2/g$, mesoporous structure and low

alumina or siliceous frame work of the supports gave a maximum efficiency to the catalyst for pesticide degradations.

- ☞ Attempts were successful in designing and development of immobilized $TiO_2$ on the zeolites/porous material photocatalysts. All are active and selective systems for respective pesticides studied in the present work using solar light.

The overall results obtained in the present study have demonstrated that combination of adsorption and photocatalytic degradation techniques in treating pollutants (here pesticides) could greatly improve the quality of the technique. This work offers the potential development capacity of the photocatalysts for designing to treat real waste water containing pesticide solutions. The salient features of all the results obtained in the present thesis work are summarized in the Table 8.1.

**Table 8.1. Salient features of combinate photocatalysts studied for the pesticide degradations▲**

| S. No. | Composite system | Support (Si/Al) | Optimum $TiO_2$ (wt%) | Surface area ($m^2/g$) at optimum loading | Isoproturon degradation | | | Technical Pirimicarb degradation (min) | Commercial pesticide degradation | | | | Publications |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Rate ($M.L^{-1}.min^{-1}$) | $t_{1/2}$ (min) | Mineralization in 5h (%) | | Imidacloprid | | Phosphamidon | | |
| | | | | | | | | | % | min. | % | min. | |
| 1 | $TiO_2$/HY | 2.6 | 10 | 130 | 5.95E-06 | 11.8 | ~ 80 | 150 | 93 | 360 | 95 | 300 | **Solar Energy Materials and Solar Cells, 92 (2008) 332-342 & 992** |
| 2 | $TiO_2$/H-MOR | 20* | 15 | 352 | 1.16E-05 | 5.71 | ~ 87 | 60 | 100 | 240 | 100 | 90 | **Journal of Hazardous Materials, In Press, 2008.** |
| 3 | $TiO_2$/AlMCM-41 | 15.5 | 10 | 742 | 6.79E-06 | 9.61 | ~ 88 | 45 | 100 | 300 | 100 | 120 | **Chemosphere, 72 (2008) 644-651** |
| 4 | $TiO_2$/PNS | - | 5 | 115 | 7.88E-06 [a]<br>2.12E-05 [b] | 8.79 [a]<br>3.52 [b] | ~ 86 [b] | 60 | 100 | 240 | 100 | 120 | **Water Research, (Communicated), 2008** |
| 5 | $TiO_2$/SBA-15 | - | 10 | 432 | 1.88E-05 | 3.75 | **~91** | **45** | 100 | **180** | 100 | **60** | **Chemosphere, In press, 2008** |

Optimum catalyst amount for S. No. 1, 3, 5 and a = 1.0 g $L^{-1}$; S. No. 2 = 1.5 g $L^{-1}$; and S. No. 4 and b = 3.0 g $L^{-1}$; * - $SiO_2/Al_2O_3$; ▲ = pH 7