CONCLUSION

Heterogeneous semiconductor photocatalysis is an advanced oxidation or degradation process to eliminate organic and dye pollutants in water. Photocatalytic reactions have received special attention in the decomposition of hazardous organic compounds because of their complete mineralization ability and possible application to pollution control using solar energy that is freely available almost throughout the year.

In the present investigation, studies were carried out on semiconductor oxides, mixed oxide solid solutions and phthalocyanines with an aim to correlate their solid state and photocatalytic properties with the substitution of different metals. The oxide samples investigated were prepared by co-precipitation method, which on sintering gave solid solutions.

X-ray studies confirmed that the prepared samples are monophasic and in well crystalline form. Ceria can form solid solution with other elements up to 30% mole maintaining cubic fluorite structure. CeO$_2$ is having cubic fluorite structure and SnO$_2$ is in tetragonal phase. All Ce$_{1-x}$Sn$_x$O$_2$ samples from $x = 0.1$ to $0.3$ are having cubic structure with decrease in lattice parameter due to introduction of small size Sn atom into the CeO$_2$ crystal lattice. Ce$_{1-x}$Fe$_x$O$_2$ from $x = 0.1$ to $0.3$ also show similar cubic fluorite structure with decrease in lattice parameter whereas Fe$_2$O$_3$ has hexagonal structure. From Ce$_{0.9}$Mn$_{0.1}$O$_2$
to $\text{Ce}_{0.7}\text{Mn}_{0.3}\text{O}_2$ show cubic fluorite structure with increase in lattice parameter due to large ionic size of Mn atoms. Similarly $\text{Sn}_{1-x}\text{Mn}_x\text{O}_2$, from $x = 0.1$ to $x = 0.3$ show tetragonal structure. Phthalocyanines have stable $\beta$ phase with square planar structures.

The FTIR is an important tool to see gradual changes taking place in the metal oxygen bonding on substitution of metal ion in the oxides. In the IR spectra of doped compounds evolution of new bands can be observed with metal substitution. The frequency of these bands has been related to the strength of metal – oxygen covalency.

In $\text{Ce}_{1-x}\text{Sn}_x\text{O}_2$ ($x = 0, 0.1, 0.2, 0.3$ and $1.0$) samples, it is observed that with the substitution of $\text{Sn}^{4+}$ in $\text{CeO}_2$ the absorption peak observed at $852\text{cm}^{-1}$ gets reduced. And there is appearance of peaks at $620$ and $670\text{ cm}^{-1}$ due to Sn-O vibrational modes. For $\text{Ce}_{1-x}\text{Fe}_x\text{O}_2$ samples, $x = 0.3$ show two sharp absorption peaks at $600$ and $652\text{ cm}^{-1}$ which are of Fe – O bond and peak at $852\text{ cm}^{-1}$ gets reduced which is of Ce-O stretching vibrational mode. The $\alpha-\text{Fe}_2\text{O}_3$ shows intense bands.

In the IR spectra of $\text{Ce}_{1-x}\text{Mn}_x\text{O}_2$ series, it is observed that as $x$ increases the Ce-O vibrational modes starts disappearing and there is evolution of Mn-O bands at $510$ and $580\text{ cm}^{-1}$. These bands are of strong intensity in $\text{Ce}_{0.7}\text{Mn}_{0.3}\text{O}_2$ than $\text{MnO}_2$. Similar observations were made regarding the IR
spectra of Sn\textsubscript{1-x}Mn\textsubscript{x}O\textsubscript{2} samples. IR spectra of phthalocyanine show absorption peaks around 1121-1123, 1090-1092, 1067-1070, 947-949, 872-885 and 754 cm\textsuperscript{-1} due to phthalocyanine skeletal vibration. In NiPc, FePc and CoPc complexes similar bands can be observed.

Thermal studies were carried out on the co-precipitated hydroxides to study their decomposition behaviour and revealed that overall decomposition pattern is similar with three distinct steps. The loss of moisture in the range of 100 - 150°C, followed by hydroxide decomposition between 150 – 350°C and initiation of a solid state diffusion leading to solid solution between 400 – 700°C. The solid solution formation appears to take place over a large range of temperature after decomposition. Phthalocyanines do not have a sharp melting point they decompose at elevated temperature. Among all the phthalocyanines under study Cobalt phthalocyanine has higher stability.

Electrical resistivity measurement with temperature showed that the resistivity pattern of all the compositions decreases exhibiting the semiconductor behaviour. CeO\textsubscript{2} and SnO\textsubscript{2} are n-type semiconductors. On doping CeO\textsubscript{2} with Sn\textsuperscript{4+} electrical resistivity increases with x and it is maximum for Ce\textsubscript{0.8}Sn\textsubscript{0.2}O\textsubscript{2}. Similarly on substituting Ce\textsuperscript{4+} with Fe\textsuperscript{3+} and Mn\textsuperscript{4+} electrical resistivity increases due to formation of oxygen vacancies. Phthalocyanines also show typical semiconductor behaviour.
Magnetic susceptibility studies showed that CeO\(_2\) is paramagnetic and SnO\(_2\) is diamagnetic. The intermediate compositions are paramagnetic and the susceptibility value decreases with the substitution of Sn. Also \(\mu_{\text{eff}}\) values decreases with Sn substitution. Similarly for Ce\(_{1-x}\)Fe\(_x\)O\(_2\), Ce\(_{1-x}\)Mn\(_x\)O\(_2\) and Sn\(_{1-x}\)Mn\(_x\)O\(_2\), the intermediate compositions are paramagnetic and the gram susceptibility value increases with \(x\). Also \(\mu_{\text{eff}}\) values found to increase with substitution of Fe and Mn metals. Among phthalocyanines, Cobalt phthalocyanine and copper phthalocyanine are paramagnetic and contains one unpaired electron. The \(\mu_{\text{eff}}\) values are slightly lower than the expected values due to contribution of direct or super exchange intermolecular interactions. Nickel phthalocyanine is diamagnetic due to planar symmetry. The saturation magnetization values showed that Fe\(_2\)O\(_3\) exhibit ferromagnetic behaviour.

ESR spectra recorded at room temperature showed broad line width for some of the recorded compositions. This may be due to the paramagnetic ions with a nuclear moment having a short lifetime of excited state because of larger size rare earth ions in the samples. ESR data are in agreement with the magnetic susceptibility data regarding the paramagnetic nature of the samples.

UV-Visible Diffuse Reflectance of the semiconductor photocatalysts was carried out to find out the band gap energies. These band gap energies were attempted to correlate with the photocatalytic activity in the
dye degradation process. Large band gap help in inhibiting electron – hole recombination.

A significant increase in the photocatalytic activity for the degradation of Naphthol Blue Black dye was observed by substitution of Sn$^{4+}$ and Fe$^{3+}$ in CeO$_2$ crystal lattice. This may be due to the enhancement of Ce$^{4+}$- Ce$^{3+}$ redox couple and improvement of band gap energy. As the $x$ increases in the series band gap is increased. However slight increase in the photocatalytic activity was observed for Mn substitution in CeO$_2$ lattice. SnO$_2$ is a good photocatalyst for the degradation of dye. Slight increase in the photocatalytic activity was observed for Mn substitution in SnO$_2$ crystal lattice. Also metal phthalocyanines show better photocatalytic activity. Among all the phthalocyanines, iron phthalocyanine has higher activity than others due to large band gap energy. The pH of the solution is an important factor in determining the photocatalytic activity.

It was found that textile diazo dye NBB can be degraded efficiently using semiconductor photocatalysts with solar light. The NBB dye degrades to a colourless solution after 240 min irradiation time. The formation of CO$_2$, NH$_4^+$, NO$_3^-$ and SO$_4^{2-}$ was evidence for the complete mineralization of the NBB dye. The mechanism involves formation of OH$^-$ radical which is an active
oxidizing agent for the degradation of NBB dye. O₂ prevents recombination of electron – hole pairs thus enhancing the reaction rate.

Also photocatalytic degradation of Auramine-O dye over selected samples showed good results. Metal phthalocyanines are good photocatalysts for the degradation of Auramine dye. Among all FePc show higher photoactivity than others due to large band gap energy which prevents electron hole recombination. For Ce₁₋ₓSnₓO₂ series, Ce₀.₈Sn₀.₂O₂ show better activity than other doped samples. CeO₂ show very little activity.

It is concluded that the photocatalytic degradation of hazardous chemical wastes and dye pollutants with semiconductor photocatalysts are economical, thermally stable and equally efficient but still the following strategies need to be considered for better performance:

1. Selection of the dopants that principally determine the photocatalytic activity.
2. Valency and vacancy control by the selection of dopants.
3. Enhancement of surface area by forming fine particles such as nano particles or dispersing on supports.
4. Improving favourable band gap either by using coupled semiconductors or by doping.
5. May be also by addition of precious metals with their appropriate regeneration to realize a high performance of the catalyst.