

Solar assisted photocatalytic degradation of methyl orange over synthesized copper, silver and tin metalloporphyrins

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The free base porphyrin, tetraphenyl porphyrin (TPP) and metalloporphyrins of Cu, Ag and Sn were synthesized and characterized by UV-Visible spectroscopy, IR spectroscopy, ¹H NMR spectroscopy and Elemental analysis. The results are discussed in the light of magnetic susceptibility, diffuse reflectance spectroscopy (DRS) and electron spin resonance spectroscopy (ESR). These porphyrins showed interesting semiconducting behaviour and were employed for trapping solar radiations for photocatalytic degradation of the azo dye methyl orange at different pH conditions. This reaction was studied as a model reaction for finding the photoactivities of these compounds.

Keywords: Metalloporphyrins, Photocatalysts, Photodegradation, Methyl orange, Organic semiconductors

Many industrial and textile processes are discharging large quantities of dye in the environment. Among the varieties of dye demanded by the various industries, azo dyes constitute up to 60-70% of the demand. During the course of production and application about 10% of them are lost in the environment as coloured effluent wastes¹. Thus the natural quality of water is degraded and a threat is posed to the environment due to water pollution. As far as the current legislation regarding wastewater in majority of the countries is concerned, it requires treatment by physical, chemical and biological methods before it is released into environment^{2,3}. It is an observed fact that very few azo-dyes are oxidized aerobically. It is also frequently seen that some of the azo-dyes are degraded anaerobically to give aromatic amines which are then degraded aerobically^{4,5}. In azo-dyes the destruction of chromophoric structure is important for the removal of colour. The sulphonate acid groups present in the structure play the role of weak auxochrome and increase the solubility of dye in water. Conventional biological treatments are also used to treat the water but due to hazardous effects of reactive dyes on microbial population, the efficiencies of these processes are reduced⁶. Under the present scenario of water pollution control, there is a need for clean, non-toxic and fresh water for the welfare of society. In this

connection oxidative degradation processes seem to be promising^{7,8}.

Heterogeneous photocatalysis by semiconductor materials is a promising technology in dealing with global pollution problems. Use of an inorganic photocatalyst such as TiO₂ is shown to be a cheaper way of removing organic compounds and pollutant gases⁹. Recently a number of researches have shown photocatalytic decomposition of dyes in the presence of UV or visible light^{10,11}. Wang *et al.*¹² carried out the photodegradation of eight commercial dyes including methyl orange (MO) in TiO₂ suspension under solar radiation. Further, Rashed and El-Amin¹³ have degraded MO using light from different sources such as a halogen lamp (1000W), a fluorescent lamp and natural sunlight. From these experiments it is proved that solar radiations are superior to other two sources in the process of photodegradation of MO. The photodegradation process of MO has also been reported by Jian-Qiu-Chen and coworkers¹⁴ with the use of Pelagite as a photocatalyst found in the East Pacific Ocean. The MO is also degraded by contact glow discharge electrolysis and eventually decomposed into inorganic carbon under an applied DC voltage of 480 V and a current of about 80 mA¹⁵.

The present studies deal with the photocatalytic degradations of methyl orange over the synthesized metalloporphyrins of copper, silver and tin using solar radiations which are abundant and freely available. Metalloporphyrins are natural prototype compounds

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having high efficiency in absorption of visible light and transforming the absorbed energy for the photochemical degradation process. The course of degradation reaction was monitored at regular intervals of time using a UV-visible spectrophotometer.

Experimental Procedure

The free base tetraphenyl porphyrin (TPP) was synthesized by reported method¹⁶. Equimolar quantities of AR grade pyrrole and bezaldehyde were refluxed in propionic acid for half an hour. The reaction mixture was cooled and washed with hot methanol followed by hot water. The purple shiny crystals of TPP were obtained with 17% yield. Purification of TPP was carried out using dry column chromatography. TPP was dissolved in AR grade CHCl_3 and then added the silica gel (100-200 mesh). The mixture was thoroughly stirred and the excess CHCl_3 was evaporated on a water bath. This is then loaded in the column of 45×3 cm diameter containing silica gel (100-200 mesh) as a column material. The top of the column was covered with cotton and pure grade CHCl_3 was used as a mobile phase. At a time 1 g of TPP was purified. The impurity of tetraphenyl chlorine (TPC) remains at the top and entire TPP gets eluted in the due course of time. The yield around 90% of purified TPP was recovered. The purity of TPP was checked on thin layer chromatography (TLC) using petroleum ether and chloroform (80: 20) and found to be pure.

The above purified TPP was used to synthesize metalloporphyrins (MTPP) by a suitable method¹⁷ and the metals used were Cu, Ag and Sn. For the synthesis of copper tetra phenyl porphyrin (CuTPP), silver tetra phenyl porphyrin (AgTPP) and tetra phenyl porphyrin tin (IV) chloride ($\text{SnTPP}^{\text{Cl}_2}$), salt of the corresponding metal in excess quantity was added to a refluxing solution of TPP in dimethyl formamide (DMF). The solution was refluxed for 15 min whereas for $\text{SnTPP}^{\text{Cl}_2}$ the time required for refluxing was 2 h. The completion of metallation reaction was confirmed by withdrawing aliquots from time to time and checking spectrophotometrically. Finally, the reaction mixture was allowed to cool and then cold water was added to the reaction mixture. This was further filtered and dried in a vacuum desiccator. The synthesized CuTPP, AgTPP and $\text{SnTPP}^{\text{Cl}_2}$ were purified by dry column chromatography. The purification method was modified by introducing gradient elution of chloroform and petroleum ether

(1:1) for CuTPP and AgTPP followed by evaporation of the solvent mixture. The $\text{SnTPP}^{\text{Cl}_2}$ was purified by using a gradient solution of chloroform and methanol (1:1) followed by evaporation of solvent mixture. In CuTPP and AgTPP recovery of pure compounds was more than 90% whereas in $\text{SnTPP}^{\text{Cl}_2}$ it was around 50%. Purity of the above metalloporphyrins was checked on TLC using chloroform and petroleum ether (4:1) and found to be very satisfactory. One gram of MTPP was purified at a time.

UV-visible spectra were recorded on Shimadzu visible spectrophotometer (model uv/2450 uv) using 10^{-4} M and 10^{-5} M concentrations of each porphyrin. IR analysis of solid porphyrins was carried out using Shimadzu IR spectrometer (model prestige/21 FTIR). ^1H NMR spectra were recorded using Varian 300 MHz model. Elemental analysis for TPP and CuTPP as the representative samples of the series were recorded on Prostar Varian C, H, N, analyzer (model Flash 1112 series EA). Magnetic susceptibility was done on a Gouy balance at room temperature employing a field of the order 8000 Gauss using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as a standard material. TG-DSC measurements were done using NETZSCH-Geratebau GmbH Thermal Analyzer (STA 409 PC) to find out the thermal stability and the decomposition temperature at different stages. Electron spin resonance (ESR) study of CuTPP and AgTPP was done using Varian E-112 X-band ESR spectrometer. Diffuse reflectance spectroscopy (DRS) study was performed to calculate band gap energies on Shimadzu visible spectrometer (model uv/2450 uv). Fluorescence studies for the samples were carried out using Shimadzu spectrofluorimeter (model RF-5301PC).

Photocatalytic degradation of methyl orange was studied using porphyrin and metalloporphyrins as photocatalysts during 11.30 to 3.30 p.m. at various pH levels with solar radiations. The concentration of 10^{-5} M methyl orange was prepared and saturated with oxygen. This reaction mixture in the closed glass reactor was kept in sunlight and the degradation reaction was studied with time at different pH conditions. The degraded reaction mixture at pH 6 and 7 was subjected to high performance liquid chromatography (HPLC) using C18 column with dimensions 250×4.6 mm and particle size 5 micrometer. The solvent system selected was methanol and water (80:20) with UV detector, which functions at 254 nm. The degraded reaction mixture

of pH 7 was then subjected to ion chromatography using cation and anion exchangers.

Results and Discussion

The porphyrins TPP, CuTPP, AgTPP and SnTPP Cl_2 were characterized by UV-visible absorption spectroscopy. The porphyrins spectra are due to $\pi - \pi^*$ transitions. The electron transitions for soret band are from $a_{1u} \rightarrow e_g$ (allowed) and for Q-band $a_{2u} \rightarrow e_g$ (forbidden). The concentrations used for soret band and Q-band were 10^{-5} M and 10^{-4} M respectively. In TPP the bands observed were at 416 nm (soret), 515, 549, 590, and 647 nm (Q-bands), whereas in CuTPP, AgTPP the number of bands is reduced to two and in SnTPP Cl_2 there are three bands in the visible region. Thus successful insertion of metal in porphyrin is confirmed by disappearance of 647 nm band and reduction in number of Q-bands as compared to TPP. A free base TPP is having two hydrogens attached to two nitrogens in the porphyrin ring which is having a rectangular geometry with D_{2h} symmetry. When metallation takes place, the geometry of the porphyrin ring becomes square with D_{4h} symmetry¹⁸. As the free base TPP is metallated the geometry becomes more symmetric and the number of absorption bands obtained is less than TPP. When a soret band wavelength is compared for the above porphyrins, bathochromic shift is observed in the following order; TPP < CuTPP < AgTPP < SnTPP Cl_2 .

The above porphyrins were further characterized by FTIR spectroscopy. A free base TPP shows medium N-H stretching vibrations at 3317 cm^{-1} . When a metal is inserted into a porphyrin ring the stretching vibrations due to N-H disappear on account of replacement of two acidic hydrogens by the metal ion. This also gives information about the presence or absence of TPP as an impurity in the corresponding metalloporphyrins. The main intense absorption band of the metal chelate of TPP appear at 1600 cm^{-1} and show $-\text{C}=\text{C}-$ stretching vibrations of phenyl rings. The strong absorption band near 1000 cm^{-1} appears due to vibration of the porphyrin ring or pyrrole units, which is sensitive to the nature of the metal ion. Further, it establishes the strength of the metal-nitrogen bonds in the TPP chelates. It is evident from the frequency values that the strength of the metal-nitrogen bond is in the following order; CuTPP < AgTPP < SnTPP Cl_2 . The strong band common to

TPP and metal chelates near 800 cm^{-1} appears due to vibration of pyrrole ring.

^1H NMR studies always reveal the three basic parameters (i) chemical shift (ii) the splitting of the absorption signal resulting from spin-spin interactions and (iii) the intensity of the absorption signal which is a measure of the number of nuclei associated with a particular line in the spectrum. In these porphyrins, TPP, SnTPP Cl_2 belong to diamagnetic class whereas CuTPP and AgTPP come under paramagnetic class. It is seen that the range of chemical shift values in paramagnetic porphyrins is on the higher side than in diamagnetic porphyrins^{19,20}. The results observed were in agreement with the literature values. The resonance due to N-H protons is not seen in metalloporphyrins which confirms complete metallation reaction.

Elemental analysis of TPP and SnTPP Cl_2 as representative samples of the series was carried out. In case of TPP, the calculated and observed results for C, H and N were 85.95 and 84.01%, 4.92 and 4.90%, and 9.10 and 8.96% respectively, whereas for SnTPP Cl_2 the results were 78.13 and 76.52%, 4.26 and 4.33%, and 8.28 and 8.16% respectively.

TG/DSC measurements show that TPP, CuTPP, AgTPP are thermally stable up to 400°C whereas SnTPP Cl_2 shows very gradual loss in weight at the beginning in synthetic air at a flow rate of 20 mL per min. This reveals that four coordinated TPP, CuTPP and AgTPP are more stable than six coordinated SnTPP Cl_2 . As there is no endothermic peak observed in TG/DSC, the melting point of these porphyrins is not confirmed. It is seen that TPP decomposes in four different stages starting at 432°C and ending at 718°C with nearly 100% weight loss²¹. The CuTPP decomposes in three different stages starting at 488°C and ending at 660°C with nearly 90% weight loss. The AgTPP decomposes in four different stages where the first decomposition temperature is 465°C and last decomposition temperature is 627°C with nearly 85% weight loss. SnTPP Cl_2 loses the weight from the beginning and shows the first decomposition at 489°C and the last decomposition temperature at 514°C with nearly 75% weight loss. Thus it is seen that free base porphyrin TPP decomposes completely whereas CuTPP, AgTPP and SnTPP Cl_2 leave some residues due to formation of respective metal oxides, which was subsequently confirmed by qualitative analysis. Fig. 1 shows TG/DSC thermogram for AgTPP as representative sample.

The magnetic susceptibility (χ_g) of the porphyrins was determined by Gouy balance at room temperature using the field strength of 8000 Gauss. Among the above synthesized samples TPP, SnTPP₂ are diamagnetic whereas CuTPP and AgTPP are paramagnetic in nature. The values of magnetic moment for CuTPP and AgTPP are 1.57 and 1.56 B.M, indicating the presence of one unpaired electron in each case. Electron spin resonance (ESR) signal of CuTPP and AgTPP were recorded at room temperature. The respective g-factor for CuTPP and AgTPP are 2.106 and 2.065 respectively. The 'g' value was used to calculate number of unpaired electrons by equation $\mu_{eff} = g\sqrt{n(n+2)}$. The hyperfine splitting constant value (A) indicates an interaction between electron spin and nuclear spin. For CuTPP and AgTPP these values were A_{II} = 200 Gauss and A_{II} = 80 Gauss respectively. Figure 2 shows ESR spectra of CuTPP as a representative sample of the porphyrins.

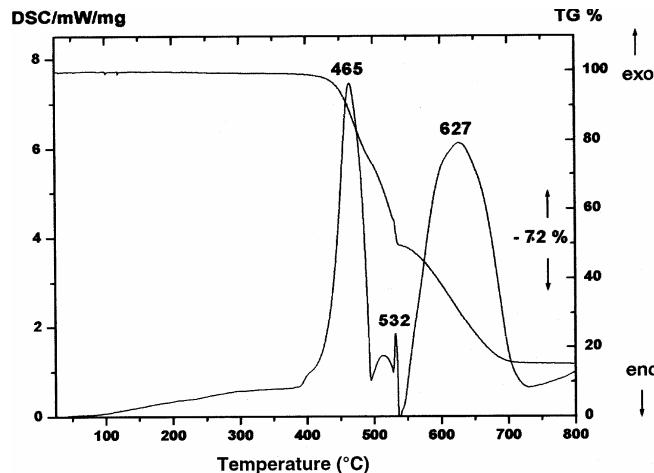


Fig. 1 — TG/DSC thermogram of AgTPP.

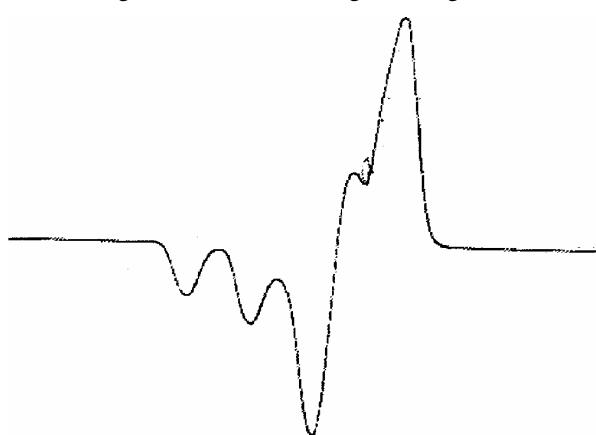


Fig. 2 — ESR spectra of CuTPP (i) Scan range 2000 G (ii) Field set 3000 G

The band gap energies of these porphyrins were calculated using diffuse reflectance spectroscopy (DRS). Figures 3 and 4 show DRS curves for CuTPP and AgTPP as representative samples. Band gap obtained for TPP, CuTPP, AgTPP and SnTPP₂ were 1.75, 1.61, 1.75 and 1.68 eV respectively. From these values it is evident that the porphyrins under investigations are comparatively low band gap metal-organic semiconductors. Therefore, it was felt worth while to test these semiconductors for photocatalytic degradation of dyes to find their photosensitivity and activity by considering a model reaction of dye degradation.

The fluorescence studies of these porphyrins were carried out at an excitation wavelength of 420 nm. Among these, TPP and SnTPP₂ are fluorescent in agreement with Hoff and Whitten²² whereas CuTPP and AgTPP are nearly non-fluorescent. Further, it is proved that the fluorescent porphyrins are more effective photocatalysts. Free base porphyrins and

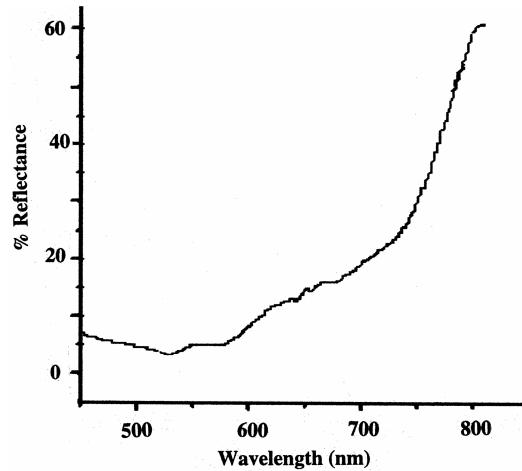


Fig. 3 — DRS spectra of CuTPP.

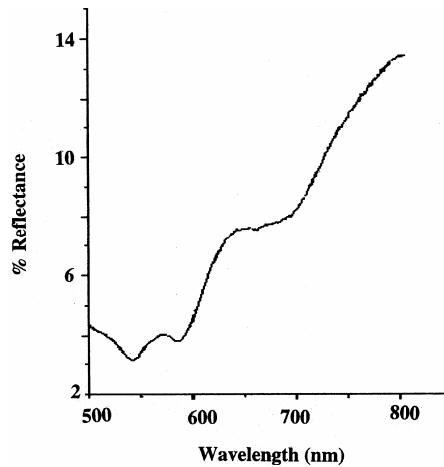


Fig. 4 — DRS spectra of AgTPP.

metalloporphyrins possess sharp and intense long wavelength electronic transitions with relatively long-lived excited states. This makes them nearly ideal photosensitive agents. In general these excited states are due to $\pi - \pi^*$ transitions and are not perturbed energetically due to the substitution of different metals. But the lifetimes and luminescence properties are influenced by the different metals²³.

Photocatalytic degradation of methyl orange was carried out using photocatalysts TPP, CuTPP, AgTPP and SnTPP Cl_2 . The UV-Visible spectrum of methyl orange at pH 6 shows $\lambda_{\text{max}} = 503$ nm, and at pH 7 as well as 10 gave $\lambda_{\text{max}} = 464$ nm. The progress of photocatalytic degradation reaction was examined by measuring absorbance at above mentioned wavelengths with time interval of 1, 2, 3, and 4 h. The above degradation reaction was optimized by taking into account different amount of catalyst, without catalyst, saturating the substrate with O₂ and without O₂, time of irradiation, use of promoter and different pH conditions like acidic, neutral and basic. The optimum amount of photocatalyst required for the photodegradation is 20 mg for 100 mL of 10⁻⁵ M methyl orange solution as shown in Fig. 5. It is also found that if the amount is exceeded 20 mg the photodegradation activity decreases²⁴. The reason is that after a saturation point the activity decreases because number of active sites on the photocatalysts as well as exposure to solar radiation per unit area decreases. It is also reported that when a photocatalyst is loaded more than optimum amount, the rate of deactivation of activated molecules increases due to collision with ground state molecules of photocatalyst²⁵.

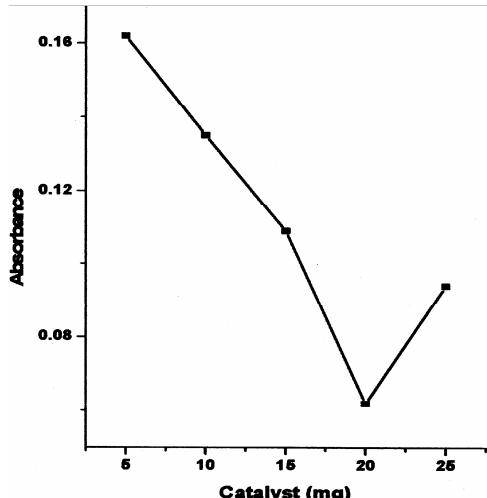


Fig. 5 — Optimization of the catalyst amount

The degradation products were analyzed by HPLC analyzer at pH 6 and 7 qualitatively. It was evident from the results that three components were present which can be qualitatively separated at different retention time on C-18 HPLC column. It is also seen that the separated components at pH 6 and 7 were identical. This explains that irrespective of pH of the degraded reaction mixture, components eluted for the same dye remain the same. It is also probable that all the components might have not separated on this column. The photodegraded reaction mixture only at pH 7 was further subjected to ion chromatography for cations and anions analysis. The quantitative analysis of degraded dye reaction mixture of methyl orange has shown the presence of Na⁺, NH₄⁺, and NO₃⁻ ions in the microgram (μg) per mL as 8.42, 0.45 and 2.78 respectively. This throws light on the process of mineralization of dye and also it gives an insight towards the rupture of bonds at particular site.

Degradation of methyl orange (MO) was studied at pH 6, 7 and 10 respectively. The results revealed that the photocatalytic activity was maximum for pH 6, good for pH 10 and minimum for pH 7. Therefore, at pH 7 only TPP and SnTPP Cl_2 were selected for photodegradation. Figures 6 - 8 show the degradation pattern of MO at different pH respectively. The photodegradation reaction was carried out for 4 h from 11.30 a.m. to 3.30 p.m. in sun light. When MO dye was degraded at pH 6, it was observed that SnTPP Cl_2 and TPP showed maximum activity whereas CuTPP and AgTPP showed minimum activity. At pH 10, the photoactivity was found to be lower than that observed at pH 6. Therefore, 0.1% of five drops of sodium lauryl sulphate (SLS) was added as a promotor. Further, even with SLS, it is observed that SnTPP Cl_2 and TPP were efficient photocatalysts whereas CuTPP and AgTPP showed low catalytic activity. Similarly at pH 7, the activity for photodegradation was low, therefore again degradation is carried out using five drops of 0.1% sodium lauryl sulphate (SLS). Here also, TPP and SnTPP Cl_2 have proved to be effective catalysts and comparable to that of inorganic semiconductor like TiO₂. It is clear that TPP and SnTPP Cl_2 are the efficient photocatalysts in the selected series. The reason attributed to this is that TPP and SnTPP Cl_2 are fluorescent porphyrins whereas CuTPP and AgTPP are nearly non-fluorescent. Since fluorescence intensity is directly proportional to the amount of solar radiations absorbed, this makes TPP and

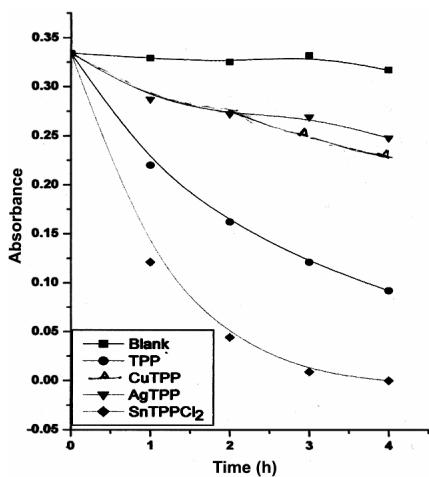


Fig. 6 — Photocatalytic degradation of Methyl orange at pH 6

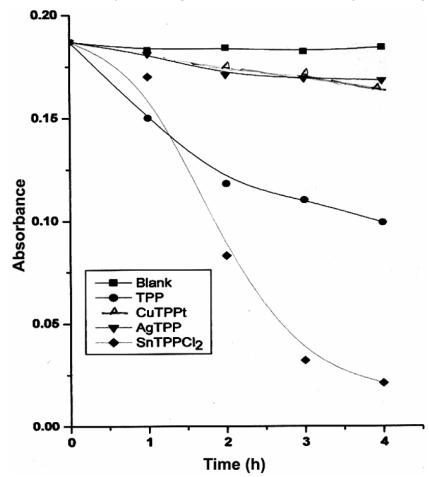


Fig. 7 — Photocatalytic degradation of Methyl orange at pH 10.

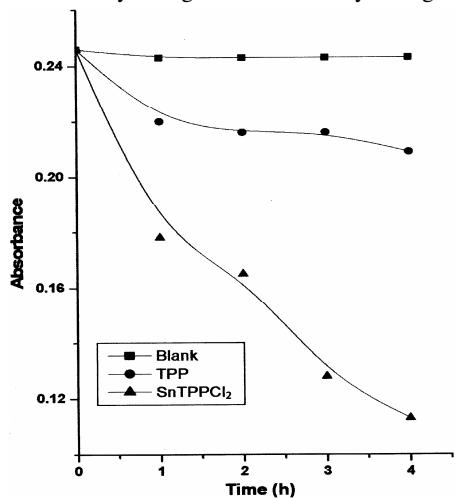
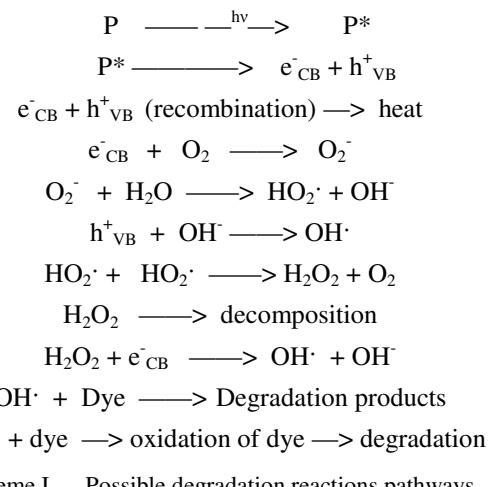


Fig. 8 — Photocatalytic degradation of Methyl orange at pH 7.

SnTPPCl₂ more effective photocatalysts. It is also observed that SnTPPCl₂ is comparatively more efficient than free base TPP as a photo catalyst. Further, it is seen that there was no change in

the chemical composition of the photocatalysts during and after photodegradation reaction. This was confirmed by UV-Visible and FTIR spectroscopy.

When solar radiations were incident upon porphyrin molecules (P) get excited (P*) and electron transfer takes place from valence band to conduction band (e⁻_{CB}) and hole in valence band (h⁺_{VB}). Porphyrins maintain relatively long-lived excited states which make them ideal photocatalysts. The oxygen present in the dye solution functions as an electron scavenger. This oxygen traps the electrons from conduction band and forms O₂⁻ species. This prevents recombination of positive holes in valence band and the electrons in conduction band. Further O₂⁻ is reacting with chemisorbed water on conduction band to produce OH and HO₂ species. The OH ions produced combines with h⁺_{VB} to form OH· radicals which are strong non-selective oxidizing agents²⁶. The hole (h⁺_{VB}) produced in the catalyst is having high oxidation potential. This may also oxidize the dye to degraded products followed by mineralization. The OH· radicals attack the chromophoric group of the dye and degrade it followed by mineralization. Thus OH· ions produced then combine with positive hole to produce OH· (free radical). Thus OH· radical is responsible for degradation of dye leading to mineralization. Presence of HO₂⁻ species was detected by ESR which is further responsible for increasing the concentration of OH· radicals. The OH· excess radicals combine to give H₂O₂ which further decomposes. Different investigators have suggested many pathways for the reaction mechanism. Based on this result following mechanism may be suggested as shown in scheme I. The radicals



(OH⁻) are responsible for breaking the bonds and rupturing the aromatic rings of the methyl orange. The sequence of opening the rings with different molecular ions is based on their molecular weights.

Conclusions

It is observed that due to TPP and SnTPP^{Cl₂}, attainment of equilibrium of a degradation reaction is faster in comparison with CuTPP and AgTPP. The above photocatalysis reaction is more efficient with the former two than the latter two compounds indicating specificity of the photocatalysts in the dye degradation reaction. It has been shown that in the degradation reaction of methyl orange at pH 10 and pH 7, the sodium lauryl sulphate (SLS) has promoted the activity of photocatalysts. Fluorescent compounds like TPP and SnTPP^{Cl₂} show better activity than non-fluorescent CuTPP and AgTPP. There was no change in the chemical composition of photocatalysts during the photodegradation reaction. The quantity of the catalyst required is small and can be recovered easily.

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