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# Solar assisted photo-catalytic degradation of Amido Black 10B over cobalt, nickel and zinc metalloporphyrins

A. V. Salker\* and S. D. Gokakakar

Department of Chemistry, Goa University, Goa-403 206, India.

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The tetraphenyl porphyrins (TPP) and metalloporphyrins such as CoTPP, NiTPP and ZnTPP were synthesized, purified and characterized by UV-Visible spectroscopy, IR spectroscopy,  $^1\text{H}$  NMR spectroscopy and elemental analysis. The results have been discussed in the light of magnetic susceptibility; diffuse reflectance spectroscopy (DRS), electron spin resonance (ESR), X-ray diffraction data and solar assisted photodegradation. The semi conducting properties of these porphyrins were employed for trapping the solar radiations for the photodegradation of azo dye such as Amido Black 10B at different pH conditions. This reaction was studied as a model reaction for finding the photoactivity of these compounds.

**Key words:** Metalloporphyrins, metal organic semiconductors, photocatalytic activity, solar assisted photodegradation, amido black 10B.

## INTRODUCTION

Many synthetic dyes are used in textile, paper, leather, ceramics, cosmetics, foods processing and ink industries (Buitron et al., 2004). The majority of these dyes are azo-dyes, which are characterized by the presence of -N = N-group. Some of these dyes are toxic and may be hazardous to human health (Saue et al., 2002; Tezcanli-Guyer et al., 2003). At the time of production and application about 10% of these dyes are lost as waste effluents (Sokmen et al., 2001). These effluent treatments involve physical, chemical and biological processes. The physical methods involve reverse osmosis, flocculation, membrane filtration and adsorption on activated charcoal (Robinson et al., 2001; McKay et al., 1999; Kannan et al., 2002).

Chemical methods involve chlorination, ozonation (Slokar et al., 1998) and degradation with mineralization. The present study is related to the photo assisted degradation of dyes leading to mineralization using synthetic metalloporphyrins as photocatalysts. It is found that, synthetic base free and metalloporphyrins are low band

gap semiconductors with efficient photocatalytic activity and prototype of natural porphyrin compounds. The field of photocatalysis is developing fast.

In the recent past, the degradation of Amido Black 10B was accomplished by Fenton oxidation process (Sun et al., 2007). Similarly, it is also degraded by aqueous suspensions of  $\text{TiO}_2$  (Qamar et al., 2005) under variety of conditions. Solar energy is a renewable source of energy which is abundant and freely available for almost eight to nine months in a year over most part of the world.

## MATERIALS AND METHODS

### Synthesis of porphyrins

The free base tetraphenyl porphyrin (TPP) was synthesized by suitable method (Adler et al., 1967). 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. Only 1 g of TPP was purified at a time. The impurity of tetraphenylchlorin (TPC) remains at the top and entire TPP gets eluted in the course of time. The recovered yield of the purified TPP was found around 90%. The purity of TPP was checked on thin layer chromatography (TLC) using petroleum ether and chloroform 80:20% and found to be highly pure.

\*Corresponding author. E-mail: [avsalker@gmail.com](mailto:avsalker@gmail.com). Tel.: (O) +91-832-6519315. Fax: +91-832-2451184.

### Synthesis of metalloporphyrins

The above purified TPP was used to synthesize metalloporphyrins (MTPP) by suitable method (Adler et al., 1970) and the metals used were Co, Ni and Zn. During synthesis the metal salts used were more than the double amount of stoichiometry and refluxed with dimethyl formamide (DMF) containing TPP in appropriate quantity at 153°C. All reactions were refluxed for 10 - 15 min. The completion of metallation reaction was confirmed by withdrawing aliquots from time to time and checking spectrophotometrically.

Further, the reaction mixture was allowed to cool and then distilled cold water was added as much as that of the reaction mixture. This was further filtered and dried in vacuum desiccators. The synthesized cobalt tetra phenyl porphyrin (CoTPP), nickel tetra phenyl porphyrin (NiTPP) and zinc tetra phenyl porphyrin (ZnTPP) were purified by dry column chromatography.

The purification method was suitably modified by introducing gradient elution which comprised of chloroform and petroleum ether 50:50% followed by evaporation of the solvent mixture. NiTPP purification process was repeated twice with the same mobile phase. In CoTPP and ZnTPP recovery of pure compounds were more than 90% whereas in NiTPP it was less than 70%. The purity of above metalloporphyrins was checked on TLC using chloroform and petroleum ether 80:20% and found to be very satisfactory. Only 1 g of MTPP was purified at a time.

### Characterization of porphyrins

UV-visible spectra were recorded on Shimadzu visible spectrophotometer (model UV/ 2450 UV) using  $10^{-4}$  and  $10^{-5}$  M concentrations for each porphyrin. FTIR analysis of solid porphyrins was carried out using Shimadzu IR spectrometer (model prestige/21 FTIR).  $^1\text{H}$  NMR spectra were recorded using Varian 300 MHz model. Elemental analysis for TPP as a representative sample of the series was recorded on Prostar Varian C, H, N, analyzer (model Flash 1112 series EA). The magnetic susceptibility ( $\chi_g$ ) was done on guoy balance at room temperature employing a field of the order 8000 Gauss using Hg [Co (SCN)<sub>4</sub>] as a standard material.

Electron spin resonance (ESR) study of CoTPP was done using Varian E-112 X-band ESR spectrometer. The X-ray diffractogram patterns for TPP and ZnTPP were recorded on ITAL-X-ray diffractometer using Cu K $\alpha$  radiation filtered through Ni. 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).

### Degradation of Amido Black 10B

Solar assisted photocatalytic degradations of azo dye Amido Black 10B were studied using solid powder porphyrins as heterogeneous photocatalysts during 11.30 a.m. to 3.30 p.m. at various pH levels. The dye degradations were always carried out in this period only. The samples of the above dye of  $10^{-5}$  M concentration in aqueous media were prepared and saturated with oxygen for 5 min. This mixture was placed in a closed glass reactor and kept in sunlight for the degradation reaction. The mixture was stirred after every 10 min. gap. The reaction was studied at different pH conditions.

The degraded reaction mixtures at pH 6 and 7 were subjected to high performance liquid chromatography (HPLC) using C18 column with dimensions 250  $\times$  4.6 mm and particle size 5  $\mu\text{m}$ . The solvent system selected was methanol and water 80:20% with UV detector, which functions at 254 nm. The degraded reaction mixture at pH 7 was then subjected to ion chromatography using cation and anion exchangers.

## RESULTS AND DISCUSSION

### UV-visible absorption analysis

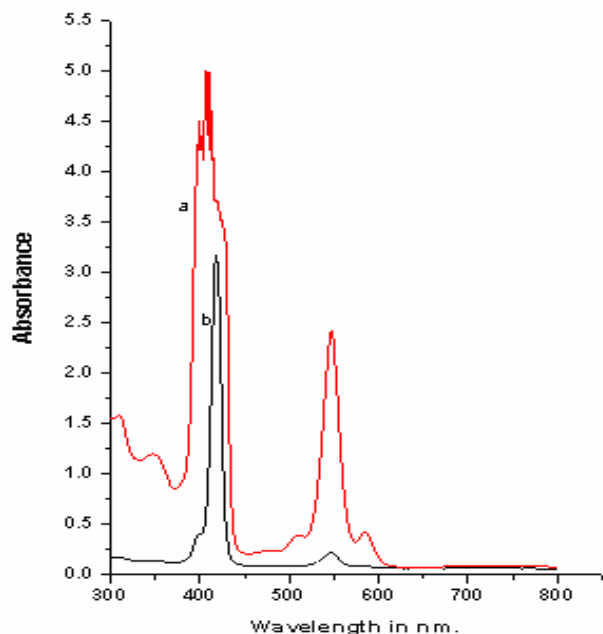
The porphyrins TPP, CoTPP, NiTPP and ZnTPP have shown the absorptions by UV-visible spectroscopy. The porphyrins spectra are due to  $\pi\text{-}\pi^*$  transitions. The electron transitions for soret band are from  $a_{1u} \rightarrow e_g$  (allowed) and for Q-band  $a_{2u} \rightarrow e_g$  (forbidden) (Dorough et al., 1951; Gouterman, 1961; Goutermann, 1978). The concentrations of  $10^{-5}$  M is used for soret band and  $10^{-4}$  M for Q-band respectively in chloroform solvent. For TPP the bands are obtained at 416 nm (soret), 515, 549, 590 and 647 nm (Q-bands) whereas in CoTPP and NiTPP the number of bands are reduced to two and for ZnTPP three in the visible region. Thus, successful insertion of metal in porphyrins is confirmed by disappearance of 647 nm band (Buchler, 1975) and reduction in number of Q-bands as compared to TPP.

The free base TPP porphyrin has two hydrogen attached to two nitrogens in the porphyrin ring which has a rectangular geometry with  $D_{2h}$  symmetry. When metallation takes place, the geometry of the porphyrin ring becomes square with  $D_{4h}$  symmetry (Marsh and Mink, 1996). The geometry of metallated TPP becomes more symmetric as a result; the number of absorption bands observed is less than free base TPP. For above porphyrins the bathochromic shift is observed in the following order of CoTPP < NiTPP < ZnTPP. Figure 1 shows UV-visible spectra of ZnTPP as the representative sample.

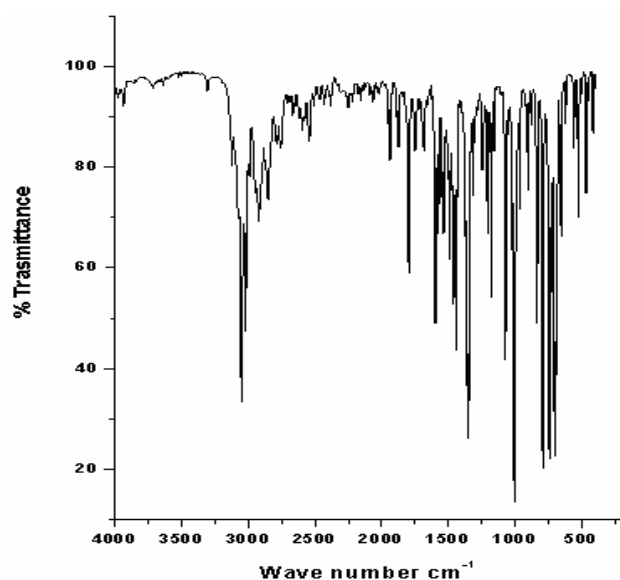
### FTIR spectroscopy

The above porphyrins have shown various absorption bands in FTIR spectroscopy. A free base TPP shows medium N-H stretching vibrations at  $3317\text{ cm}^{-1}$ . When a metal ion 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. Figure 2 shows FTIR spectra of NiTPP as a representative sample. The main prominent absorption bands of the metal chelates of TPP appear at  $1600\text{ cm}^{-1}$  and shows -C = C- stretching vibrations of phenyl rings. The frequency shift is in the order of NiTPP > CoTPP > TPP, ZnTPP.

The strong absorption band near  $1000\text{ cm}^{-1}$  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 of NiTPP > CoTPP > ZnTPP. The strong band common to TPP and metal chelates near  $800\text{ cm}^{-1}$  appears due to vibration of pyrrole ring (Thomas and Martell, 1959).



**Figure 1.** UV-Visible spectra of ZnTPP, (a)  $10^{-4}$  M and (b)  $10^{-5}$  M concentration in Chloroform.

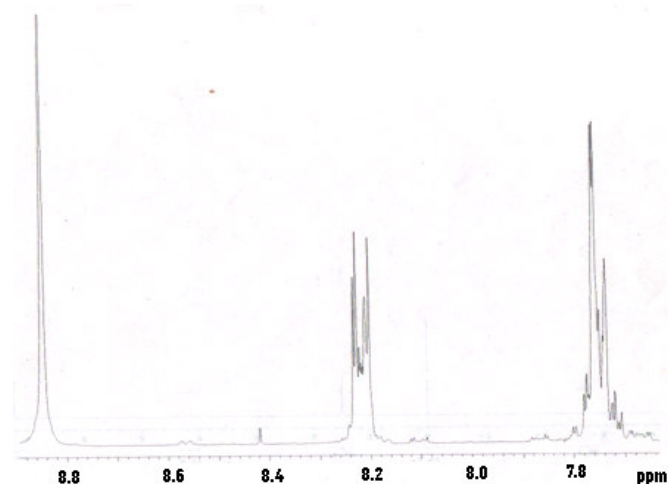


**Figure 2.** IR spectra of NiTPP.

### NMR spectroscopy

$^1\text{H}$  NMR study reveals the three basic parameters:

- (i) Chemical shift.
- (ii) The splitting of the absorption signal resulting from spin-spin interactions.
- (iii) The intensity of the absorption signal which is a measure of the number of nuclei associated with a particular line in the spectrum (Janso and Katz, 1979).



**Figure 3.**  $^1\text{H}$  NMR spectra of TPP.

In the above synthesized porphyrins, TPP, NiTPP and ZnTPP belong to a diamagnetic class whereas CoTPP fall under a paramagnetic class. The TPP a base free porphyrin gives one singlet for  $\beta$ -pyrrole protons and one singlet for N-H protons. The phenyl protons can be assigned to two resonances with little fine structure, one result from ortho protons and the other from the meta and para protons for TPP is shown in Figure 3.

In case of NiTPP and ZnTPP all the above resonances are obtained, in CoTPP the range of the chemical shift values are much larger than above diamagnetic porphyrins (Shirazi et al., 1982). The resonance due to N-H protons is not seen in metalloporphyrins which confirms the complete metallation reaction. Table 1 shows the proton NMR chemical shifts for the respective porphyrins.

### Elemental analysis

Elemental analysis of TPP as a representative sample of the series is shown below:

Elements	%C	%H	%N
Calculated	85.95	4.92	9.10
Found	84.01	4.90	8.96

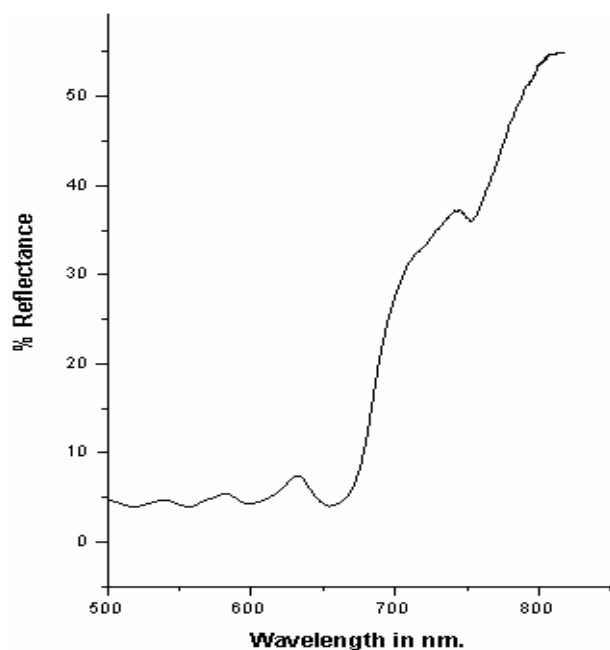
The results are fairly in good agreement and confirm the formation of the compound.

### Magnetic susceptibility and ESR studies

The magnetic susceptibility study indicated that the porphyrin samples of TPP, NiTPP and ZnTPP are diamagnetic whereas CoTPP is paramagnetic in nature. CoTPP has magnetic susceptibility  $2.25 \times 10^{-6}$  cgs units, magnetic moment  $\mu_{\text{eff}} = 1.924$  B.M. and it contains one unpaired electron (Eaton and Eaton, 1980). Electron spin resonance signal for CoTPP at room temperature is not

**Table 1.** Proton NMR chemical shifts (in  $\delta$  ppm) and DRS band gap energy (in eV) for porphyrin.

Sr. No.	Porphyrin	o-Phenyl	m- Phenyl	p-Phenyl	B-Pyrrole	Band gap Energy (eV)
1	TPP	8.22	7.74	7.74	8.84	1.75
2	CoTPP	13.8	9.88	9.67	15.9	1.92
3	NiTPP	8.0	7.7	7.7	8.7	1.82
4	ZnTPP	8.2	7.71	7.71	8.9	1.86

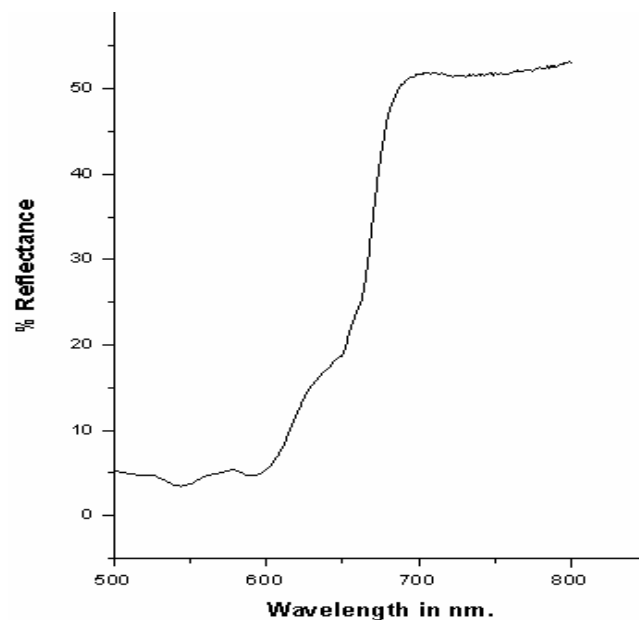
**Figure 4.** DRS spectra of TPP.

obtained therefore; it is subjected to liquid nitrogen temperature. It gave spectroscopic splitting factor  $g = 2.269$ , line width = 110 Gauss and hyperfine splitting constant  $A_{II} = 130$  Gauss. The hyperfine constant value indicates an interaction between electron spin and nuclear spin. The line width explains the life time of the excited state of the nuclear spin (Dutta and Syamal, 1993; Khrapov et al., 1974).

### Diffuse reflectance spectroscopy

The band gap energies of these porphyrins calculated by using DRS are shown in table 1. Then Figures 4 and 5 show DRS spectra for TPP and ZnTPP powders as representative samples. Band gap obtained for these compounds are in the range 1.75 - 1.92 eV as shown in Table 1. From these values it is evident that the porphyrins under investigations are comparatively low band gap metal-organic semiconductors.

Therefore, it is felt worth while to test these semiconductors for photocatalytic degradation of dyes to find their photosensitivity and activity by employing a model reaction of azo dye degradation. The porphyrins are pigments and highly coloured compounds, the DRS spectra

**Figure 5.** DRS spectra of ZnTPP.

of solids also showed some absorption peaks which are matching with the absorption peaks in solution but with some shift in their  $\lambda$  values and therefore the spectral curve are not sharp (Ozgun et al., 2005; Aoki, 2000)].

### X-ray diffraction

X-ray powder diffractogram pattern (XRD) for ZnTPP as representative sample have shown in Figure 6, indicating that these porphyrins are polycrystalline and monophasic in nature (Scheidt, 1978).

### Fluorescence studies

The fluorescence studies of these porphyrins were carried out at an excitation wavelength of 420 nm. Among these, TPP and ZnTPP are fluorescent (Hoff and Whitten, 1975) whereas CoTPP and NiTPP are nearly non-fluorescent. Further, this has proved that fluorescent porphyrins are effective photocatalysts than non-fluorescent photocatalysts in the photodegradation process. Free base porphyrins and metalloporphyrins possess sharp and intense long wavelength electronic transitions with relatively long lived excited states. This makes them nearly ideal photosensitive agents.

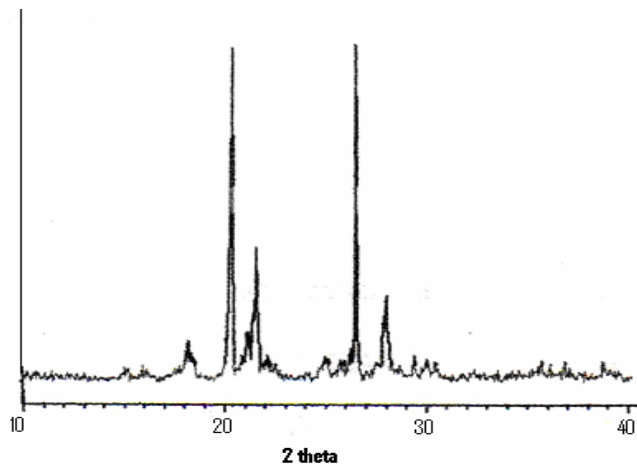


Figure 6. XRD pattern of ZnTPP.

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 different metals influence the lifetimes and luminescence properties of the porphyrins (Hoff and Whitten, 1978; Mauzerall, 1978).

### Photodegradation reaction

Photodegradations of Amido Black 10B dye were carried out using solid powder of TPP, CoTPP, NiTPP and ZnTPP as heterogenous photocatalysts in the glass reactor. The UV-Visible spectrum of Amido Black 10B at pH 6, 7 and 10 shows  $\lambda_{max} = 618$  nm in aqueous media. These porphyrins are not soluble in aqueous media. The progress of photocatalytic degradation reaction in aqueous media is examined by measuring absorbance at above mentioned wavelengths with time interval of 1, 2, 3 and 4 h. The above degradation reactions are optimized by taking into account the different parameters such as amount of the catalysts, without catalysts, saturating reaction mixture with  $O_2$  and without  $O_2$ , 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 found to be 25 mg for 100 mL of  $10^{-5}$  M Amido Black 10B solution as shown in Figure 7. It is also noticed that if the amount is exceeded 25 mg, the photodegradation activity decreases (Kartal et al., 2001). The reason for this is that, after a saturation point activity unit area decreases (Borker and Salker, 2006). It is also reported that, when a photocatalyst is not loaded with the optimum amount then the rate of deactivation of activated molecules increases due to collision with ground state molecules of photocatalyst (Saktivel et al., 2002).

### HPLC analysis

The degradation products were analyzed by HPLC

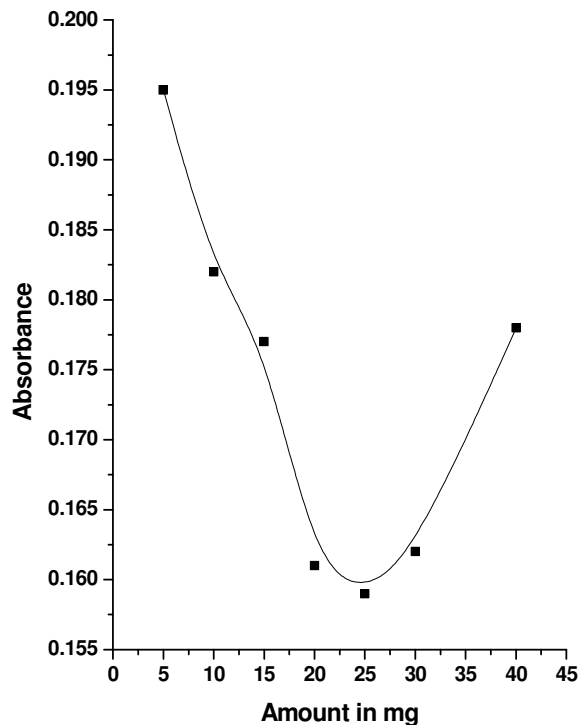


Figure 7. Optimization of the catalyst amount.

analyzer at pH 6 and 7 to find the number of degraded components resulted after degradation. It is evident from decreases because the number of active sites on the photocatalysts as well as exposure to solar radiation per the results that three components are found present which could be separated at different retention time using C-18 column. Perhaps all the components might have not been separated on this column. It is also seen that the separated components at pH 6 and 7 are identical and separated almost at the same retention times. This explains that irrespective of pH conditions of the degraded reaction mixture, the components eluted for the particular dye remains the same.

### Ion chromatography analysis

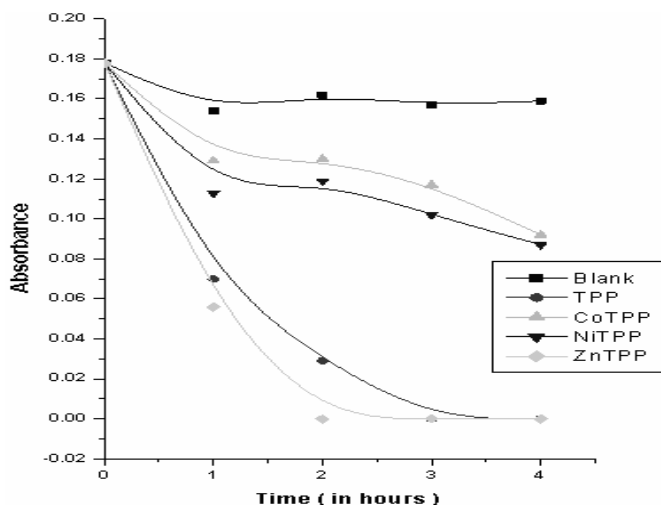
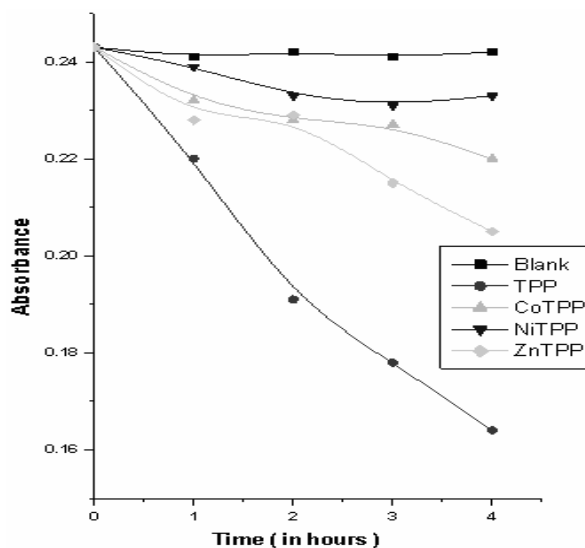
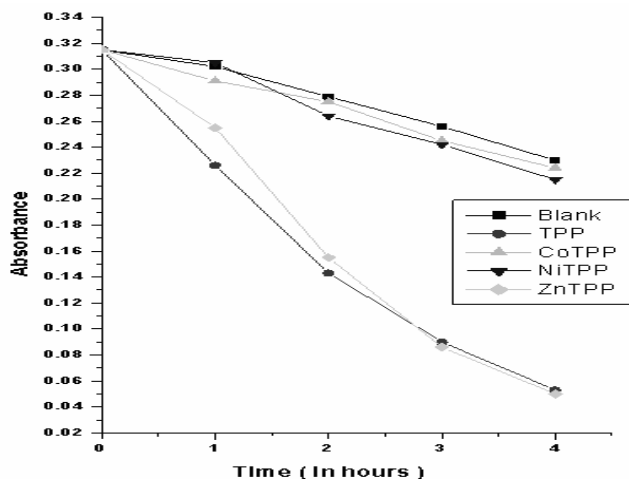
Photodegraded reaction mixture at pH 7 was further subjected to ion chromatography for cations and anions analysis. After photo-degradation of Amido Black 10B, the reaction mixture has shown the presence of  $Na^+$ ,  $NH_4^+$ ,  $NO_3^-$  and  $SO_4^{2-}$  ions as indicated in Table 2. This shades light on the process of mineralization of dyes and also it gives an insight towards the rupture of bonds at particular sites.

### Photodegradation analysis

Degradation of Amido Black 10B was studied at pH 6, 7 and 10 respectively. The recorded results reveal that

**Table 2.** Ion chromatography result.

Sr. No.	Dye	Cation conc. ( $\mu\text{g}$ )			Anion conc. ( $\mu\text{g}$ )		
		$\text{Na}^+$	$\text{NH}_4^+$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{NO}_2^-$
1	Amido Black (blank)	-	-	-	-	-	-
2	Amido Black (degraded)	9.88	0.59	-	2.11	0.50	-

**Figure 8.** Photocatalytic degradation of Amido Black 10B at pH 6 in aqueous media.**Figure 10.** Photocatalytic degradation of Amido Black 10B at pH 7 in aqueous with SLS.**Figure 9.** Photocatalytic degradation of Amido Black 10B at pH 10 in aqueous media.

photocatalytic activity is maximum for pH 6, good for pH 10 and minimum for pH 7 as shown in Figures 8, 9 and 10 respectively. The photodegradation reactions were carried out for 1 to 4 h in solar radiations during 11.30 a.m. to 3.30 p.m. When Amido Black 10B dye is - at pH 6, it is seen that the TPP and ZnTPP showed maximum activity whereas NiTPP and CoTPP showed minimum activity. For pH 10, when the same dye is degraded,

ZnTPP and TPP gave efficient photocatalytic activity whereas NiTPP and CoTPP showed low activity.

The blank solution also showed little degradation, may be due to presence of hydroxyl ions at pH 10. At pH 7 showed lower activities, therefore degradation is carried out using five drops of 0.1% sodium lauryl sulphate (SLS) as a promoter. In this context, TPP and ZnTPP have proved to be effective catalysts in comparison with CoTPP and NiTPP with SLS. From this discussion, it is evident that the magnitude of photocatalytic activity is maximum for pH 6, good for pH 10 and minimum for pH 7. Similarly, it is also clear that TPP and ZnTPP are the most efficient photocatalysts in this selected series.

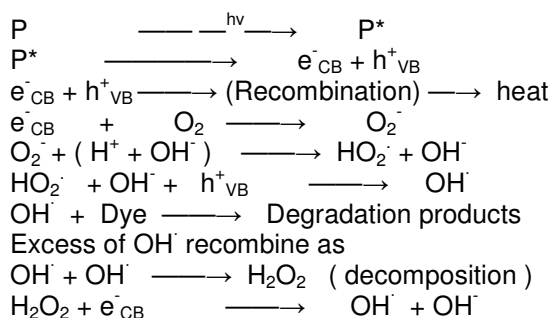
The reason for this may be attributed to the fact that, TPP and ZnTPP are fluorescent porphyrins whereas CoTPP and NiTPP are nearly non-fluorescent. Since fluorescence intensity is directly proportional to the amount of solar radiations absorbed, this makes TPP and ZnTPP more effective photocatalysts. Further, to check the reproducibility of catalytic activity, TPP as a representative sample of the series is recycled for three times. It is observed that with the successive use of TPP, its activity has decreased for the second cycle and subsequently remained almost constants for the remaining cycles. It is also revealed that there is no change in the chemical composition of the photocatalysts after photodegradation reaction and is confirmed by UV-Visible and

FTIR spectroscopy analysis.

Solar radiations when incident on porphyrin molecules get excited ( $P^*$ ) and electron transfer takes place from valance band to conduction band ( $e^-_{CB}$ ) and hole is created in valance 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  $O_2^-$  species. This prevents recombination of positive holes in valance band and the electrons in conduction band.

Further  $O_2^-$  is reacting with chemisorbed water on conduction band to produce  $OH^\cdot$  and  $OH^-$  with the liberation of oxygen. Thus,  $OH^\cdot$  ions produced then combine with positive hole to produce  $OH^\cdot$  (free radical). Thus,  $OH^\cdot$  radical is responsible for the degradation of dye leading to mineralization. The degradation reaction at pH 6 is quite faster. This may be explained on the basis of formation of  $HO_2^\cdot$  species detected by ESR (Bard, 1980), which are responsible for increased concentration of  $OH^\cdot$  radical and thus comparatively faster degradation of dye.

Excess of  $OH^\cdot$  radicals recombine may be to produce  $H_2O_2$  which further decomposes. Different investigators have suggested many pathways for the reaction mechanism. As per present study, solar radiations excite porphyrin molecule 'P' and may follow as one of the reaction paths as shown in Scheme I. (Borker and Salker, 2006).



**Scheme 1.**

## Conclusion

It is observed that due to TPP and ZnTPP, attainment of equilibrium of a degradation reaction is faster in comparison with CoTPP and NiTPP disclosing the specificity of the photocatalysts in the dye degradation reaction. In the case of degradation reaction of Amido Black 10B at pH 7, sodium lauryl sulphate has promoted the activity of degradation. Fluorescent compounds like TPP and ZnTPP show better activity than non-fluorescent CoTPP and NiTPP. There is no change in the chemical composition of photocatalysts after photodegradation reaction. These porphyrins are found to be metal organic semiconductors with low band gap energy. Solar energy is sufficient to promote photocatalytic degradation over semiconducting materials including porphyrins.

## ACKNOWLEDGEMENT

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## REFERENCES

- Adler AD, Longo FR, Finarelli JD (1967). A simplified synthesis for meso - Tetraphenylporphyrin. *J. Org. chem.* 32: 476.
- Adler AD, Longo FR, Kampas F, Kim J (1970). On the preparation of Metalloporphyrins. *J. Inorg. Nuclear Chem.* 32: 2443-2445.
- Aoki T, Hatanaka Y, Look DC (2000). *Appl. Phys. Lett.* 76: 3257-3259.
- Bard AJ (1980). *Photoelectrochemistry.* Science 207: 139-144.
- Borker P, Salker AV (2006). Photocatalytic degradation of textile azo dye over  $Ce_{1-x}Sn_xO_2$  series. *Mater. Sci. Engg. B* 133: 55-60.
- Buchler JW (1975). *Porphyrins and Metalloporphyrins*, (Eds), Smith K.M., Elsevier, Amsterdam, Chapter 5: 187-189.
- Buitron CL, Quezada M, Moreno G (2004). Aerobic degradation of the azo dye acid red 151 in a sequencing batch biofilter. *Bioresource Technol.* 92: 143-149.
- Dorough GD, Miller JR, Huennekens FM (1951). Spectra of the metallo-derivatives of  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  - tetraphenylporphine. *J. Am. Chem. Soc.* 73: 4315-4320.
- Dutta RL, Syamal A (1993). *Elements of Magnetochemistry* (2<sup>nd</sup> Eds), Affiliated East-west Press Pvt Ltd. Chapter 12: 206-211.
- Eaton SS, Eaton GR (1980). *Inorg. Chem.* 19: 1095-1096.
- Gouterman M (1961). Spectra of porphyrins. *J. Mol. Spectros.* 6: 139-144.
- Gouterman M (1978). *The Porphyrin*, (Eds), Dolphin D, Vol. III, Academic Press, New York, Chapter 1: 89-98.
- Hoff FR, Whitten DG (1975). *Porphyrins and Metalloporphyrins*, (Eds), Smith KM, Elsevier, Amsterdam, Chapter 16: 667-668.
- Hoff FR, Whitten DG (1978). *Porphyrins*: (Eds), Dolphin D, Vol. II, Academic Press, New York, Chapter 6: 161-162.
- Janson TR, Katz JJ (1979). *The Porphyrins*, (Eds), Dolphin D, Vol. IV, Academic Press, New York, Chapter 1: 3-9.
- Kannan N, Meenakshisundaram M (2002). Adsorption of Congo Red on various activated carbons: a comparative study. *Water Air and Soil Pollut.* 138: 289-305.
- Kartal OE, Erol M, Oguz H (2001). Photocatalytic destruction of phenol by  $TiO_2$  Powders. *Chem. Technol.* 24: 645-649.
- Khrapov VV, Ginzburg SF, Burtseva LN, Stanko VI (1974). *J. Theoretical and Experimental Chemistry.* 8: 336-339.
- Marsh DF, Mink LM (1996). Microscale synthesis and electronic absorption spectroscopy of tetraphenyle porphyrin and metalloporphyrins. *J. Chem. Educ.* 73: 1188-1190.
- Mauzerall DI (1978). *The Porphyrins*. (Eds), Dolphin D Vol V, Academic Press, New York, Chapter 2: 29-31.
- Mckay G, Porter JF, Prasad GR (1999). The removal of dye colours from aqueous solutions by adsorption on low cost materials. *Water Air Soil Pollut.* 114: 423-438.
- Ozgun U (2005). *J. Appl. Phys.* 98: 041-301.
- Qamar M, Saquib MMuneer M (2005). Photocatalytic degradation of two selected dye derivatives, chromotrope 2B and Amido Black 10B, in aqueous suspensions of titanium dioxide. *Dyes Pigments* 65: 1-9.
- Robinson T, Mc Mullan G, Marchant R, Nigam P (2001). Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresource Technol.* 77: 247-255.
- Sakthivel S, Geissen SV, Bahnemann DW, Murugesan V, Vogelpohl A (2002). Enhancement of photocatalytic activity by semiconductor heterojunctions:  $\alpha$ -  $Fe_2O_3$ ,  $WO_3$  and CdS deposited on ZnO. *J. Photochem. Photobiol. A.* 148: 283-293.
- Saue T, Neto GC, Jose HJ, Moreira RFPM (2002). Kinetics of photocatalytic degradation of reactive dyes in a  $TiO_2$  slurry reactor. *J. Photochem. Photobiol. A* 149: 147-154.
- Scheidt WR (1978). *The Porphyrins*. (Eds), Dolphin D Vol III, Academic Press, New York, Chapter 10: 480-483.
- Shirazi A, Goff HM (1982). Carbon 13 and proton NMR spectroscopy of four and five coordinated cobalt (II) porphyrins. *Inorg.*

- Chem. 21: 3420.
- Slokar YM, Majcen Le Marechal A (1998) Methods of decolouration of textile waste waters. *Dyes & Pigments* 37: 335-356.
- Sokmen M, Allen DW, Akkas F, Kartal N, Acar F (2001) Photodegradation of some dyes using Ag-loaded Titanium dioxide, *Water, Air and Soil Pollut.* 132: 153-163.
- Sun J, Sun S, Wang G, Qiao L (2007). Degradation of azo dye Amido Black 10B in aqueous solution by Fenton oxidation process. *Dyes & Pigments* 74: 647-652.
- Tezcanli-Guyer G, Ince NH (2003). Degradation and toxicity reduction of textile dyestuff by ultrasound. *Ultrasonics Sonochem.* 10: 235-240.
- Thomas DW, Martell AE (1959). Metal chelates of tetraphenyl porphine and some p-substituted derivatives. *J. Am. Chem. Soc.* 81: 5111-5119.