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Photocatalytic Degradation of Rhodamine B using Aqueous Free-Base Porphyrin and Metalloporphyrins of Mn, Fe and Sn

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The aqueous-porphyrins used in clinical studies for photodynamic therapy (PDT) are exploited as the photocatalysts for the first time in the photodegradation of rhodamine B in the acetone medium. The porphyrins such as free-base porphyrin $TPPS_4$ and $MnTPPS_4Cl$, $FeTPPS_4Cl$, a dimer $(FeTPPS_4)_2$-O and $SnTPPS_4Cl_2$ were synthesized and characterized by ultraviolet-visible, infrared, ^1H NMR, fluorescence spectroscopies and elemental analysis. The band-gap energies of the respective porphyrins were determined using DRS spectroscopy. They have shown 100% degradation of the dye within 25-40 min, which was confirmed by HPLC and ion-chromatography. This has revealed that semiconductor aqueous-porphyrins may be a good choice as photocatalysts in the photodegradation of rhodamine B dye.

Keywords: Metalloporphyrins, Trivalent, Tetravalent metal ions, Photodegradation, Ion chromatography, Rhodamine B dye.

INTRODUCTION

With the advent of industrial revolution, material prosperity has increased in all walks of life and slowly started worsening the quality of soil, water and air. The pollutants responsible for this change in the natural quality of environment are in huge numbers from synthetic textile dyes, industrial dyestuffs and the concerned effluents discharged from the textile industries from time to time [1-3].

To overcome the situation, when different varieties of methods are attempted by many research workers. They include physical methods such as reverse osmosis, flocculation or coagulation but it is proved that they are responsible in the production of secondary products [4]. The application of biological methods has proved that large quantity of sludge is produced and created a disposal problem. Equally, in these methods the other properties like temperature and pH control play an important role [5-7]. Practically speaking, chemical methods are much more effective but their long-time treatment, small quantity of effluent requirement and subsequently higher cost are the basic problems.

To remedy this problem, a way out discovered was advanced oxidation process (AOP), where contaminants or organic impurities are non-selectively and rapidly oxidized [8-10]. Advanced oxidation process involves the generation of hydroxyl radicals ($^•OH$) free radicals, which are non-selective strong oxidizing agents, responsible for the oxidation of large quantities of organic pollutants present in the dye solution. The advantage of ($^•OH$) free radical is, it possesses the high oxidation potential (2.80 V) which is higher next to fluorine (3.03 V). but fluorine is toxic in nature, therefore, cannot be used. Thus, $^•OH$ radicals which are promising non-toxic free radicals are widely used in the AOP. The methods used for generation of hydroxyl radicals are *viz.* by the use of hydrogen peroxide (H_2O_2), ozone (O_3), iron salts (Fenton oxidation) and semiconductor photocatalysts using either UV or visible radiation. Further, these generated $^•OH$ react with organic pollutants in the dye and transform them into CO_2 and H_2O with mineralization by destroying the chromophoric groups [11].

The frequent use of semiconductor TiO_2 as a photocatalyst which is employed in the photodegradation of organic pollutants [12,13], gas sensors [14], solar cells [15] and even for the production of hydrogen in the process of water splitting [16]. In the recent past, there have been extensive experiments, where, a thin film of titania powders is used very often [17-21]. Various metals such as V, Cr, Fe, Co, Ni Cu, Zn from first transition series, Zr and Mo from second transition series and Ce and Nd from lanthanide series are also used to dope anatase to reduce the band gap between valence band and conduction band and subsequently to prevent the recombination of electron hole pair [22-27].

The objective of the present study is the photodegradation of rhodamine B, a xanthene type dye, using self-synthesized sulphonated aqueous-porphyrins as photocatalysts in presence of solar radiation. The tremendous growth and development of aqueous free-base porphyrin and their metalloporphyrins have been seen during last three decades. The porphyrins are widely as well as extensively used in the models and mimics of enzymes such as peroxidases, catalase, P-450 cytochromes or trans membrane electron transport agents. As a special and typical molecule, porphyrins possess distinctive, reversible oxidation and reduction chemistry that encourages use as wires, switches, transistors, junctions, and photodiodes [28-31]. It is also to be noted that the porphyrins such as tetra(4-carboxy phenyl)porphyrin (TCPP), Cu-5-mono [4-(2-ethyl-p-hydroxy benzoate) ethoxyl-10,15,20 tetraphenyl porphyrin (CuPp), have been used as coating material on TiO_2, ZnO, CuO for the degradation of dyes very frequently. Monomeric, dimeric and oligomeric lignin model compounds were extensively degraded by metalloporphyrins both in organic solvents and water [32,33]. In present study, neither we require, oxidizing agents such as H_2O_2, $K_2S_2O_8$, ozone or Fenton oxidation mechanism nor we have coated the porphyrins on the semiconductor materials such as TiO_2, ZnS, CdS or SnO_2 but exclusively, a small quantity of porphyrins were used (5 mg) to degrade the dye, which results in the complete degradation of rhodamine B dye within 25-40 min.

EXPERIMENTAL

A free-base non-aqueous tetraphenyl porphyrin (TPP) is a precursor for the preparation of sulphonated free-base porphyrin called as tetra sodium *meso*-tetra(*p*-sulphonato phenyl) porphyrin ($TPPS_4$) was obtained by synthetic route of standard method [34]. The stoichiometric proportions used were 0.003 mole of TPP and 0.5 mol of conc. H_2SO_4, refluxed for 8 h in a reaction assembly and kept aside for 48 h with no disturbance. The reaction mixture was further diluted with distilled water followed by heating with CaO (lime) till the entire solution attains purple colour. Further, the solution was filtered for the removal of $CaSO_4$, subsequently washed with hot water and concentrated to about 150-200 mL. The next step was the addition of Na_2CO_3 to maintain the pH of the solution in the vicinity of 8-10 h. At this stage, the precipitated $CaCO_3$ was removed by filtration and 90% ethyl alcohol was added with the regular interval of time. The filtrate was then subjected to concentration on steam bath and dried in an electric oven at 100 ºC for 2 h. The crystals of obtained $TPPS_4$ were preserved in an air tight capsule, since they are deliquescent in nature. The crystals of $TPPS_4$ were purified by dry column chromatography, where, basic alumina was a stationary phase and a mixture of water, methanol and acetone were used in 7:2:1 proportion as a mobile phase. The column shows two types of colours *i.e.*, green colour due to dication (rejected) and purple coloured fraction, which was selected, concentrated and dried in a vacuum desiccator as $TPPS_4$.

The purified form of $TPPS_4$ was used as a precursor for the preparation of trivalent and tetravalent metalloporphyrins. The synthesis of trivalent metal porphyrin $FeTPPS_4Cl$ and its dimer $[O\text{-}(FeTPPS_4)_2]$ was carried out using method [34], whereas synthesis of $MnTPPS_4Cl$ was done by addition of slight excess of metal salt than stoichiometric requirement in the above procedure. The synthesis of tetravalent metal porphyrin $SnTPPS_4Cl_2$ was accomplished by addition of tenfold excess of metal salt to the aqueous solution of $TPPS_4$ and then above procedure was repeated. The method of dry column chromatography was used for the purification of all synthesized porphyrins. There were three types of bands available on the column *viz.* green coloured band due to dication $[H_4(TPPS_4)^{2+}]$, specific coloured band due to respective porphyrin and colourless band due to unreacted salt of the corresponding metal. The fraction due to corresponding metalloporphyrin was checked on the spectrophotometer and selected. In general, the recovery of purified metalloporphyrins was found in the range of 80-85%. The above mentioned metalloporphyrins required metal salts in excess quantities than stoichiometric requirement. The purity of above metalloporphyrins was checked on TLC using a mixture of methanol, ammonia and petroleum ether in the ratio 5:40:55. The recovered compounds exhibited a satisfactory purity.

A Shimadzu spectrophotometer (model UV/2450UV) was used to record the characteristic absorption bands of free-base and other metalloporphyrins in the Soret region and visible region. The Shimadzu spectrometer (Prestige/21FTIR) was used to record the IR spectra of the solid deliquescent porphyrins. Varian 300 MHz model was used to record proton NMR spectra of the above synthesized compounds. The band-gap energy of respective porphyrin in solid state was measured using Diffused Reflectance Spectroscopy (DRS) using Shimadzu UV-visible spectrophotometer (UV/2450 UV). The fluorescence intensity was measured on a single beam Shimadzu spectrofluorimeter (RF-5301PC). The results of elemental analysis of aqueous porphyrins were recorded on Prostar Varian C, H, N analyzer (Flash 1112 series EA) for $MnTPPS_4Cl$ as a representative sample. The magnetic susceptibility 'χ_g' of all porphyrins was measured in air at room temperature using Gouy balance method, which was used for the calculation of magnetic moment. The magnetic field employed was 8000 Gauss and the single pan analytical balance of DONA was used.

Photodegradation of rhodamine B dye: A solution of rhodamine B dye (10^{-5} M) was subjected to photocatalysis in acetone medium and solar radiation were induced in a reactor for further reaction. The pure acetone for experiment was obtained by refluxing AR grade acetone with $KMnO_4$ for 2 h followed by distillation. The rhodamine B dye solution was degraded in sunlight at the regular interval of 5 min. The HPLC analysis of the degraded reaction mixture was carried using Perkin-Elmer SERIES-200 with C18 column of dimensions 250 × 4.6 mm and particle size 5 µm. The solvent phase selected was methanol and water in the ratio 80:20%. The mineralization study of same solution was done using ion-chromatography on Shodex-CDS 5 analyzer.

RESULTS AND DISCUSSION

UV-visible studies: The aqueous free-base porphyrin $TPPS_4$ and $MnTPPS_4Cl$, $FeTPPS_4Cl$, a dimer $(FeTPPS_4)_2$-O, and $SnTPPS_4Cl_2$ were characterized with respect to their characteristic Soret band and visible region bands. An intense Soret bands range from 394-418 nm for $FeTPPS_4Cl$ to $SnTPPS_4Cl_2$ were observed (Table-1). The bands in the visible region for free-base $TPPS_4$ are observed at 516, 553, 579 and 633 nm. For other metalloporphyrins, the bands in the visible region were 516- 644 nm, where in some porphyrins, the band around 516-528 disappears, while in $(FeTPPS_4)_2$-O and $SnTPPS_4Cl_2$ the last band around 644 nm disappears after insertion of the metal in the porphyrin moiety. Therefore, for each porphyrin some bands are common and some are disappearing as compared with $TPPS_4$ [35,36]. Fig. 1 shows the overlay of the necessary absorption bands for all synthesized porphyrins.

TABLE-1
UV-VISIBLE ABSORPTION PEAKS IN SORET AND Q-BANDS

Porphyrin	Absorption bands (nm)				
	Soret band	Q-bands			
$TPPS_4$	413	516	552	579	633
$MnTPPS_4Cl$	413	516	553	577	644
$FeTPPS_4Cl$	394	–	528	608	644
$(FeTPPS_4)_2$-O	395	–	567	609	–
$SnTPPS_4Cl_2$	418	515	553	593	–

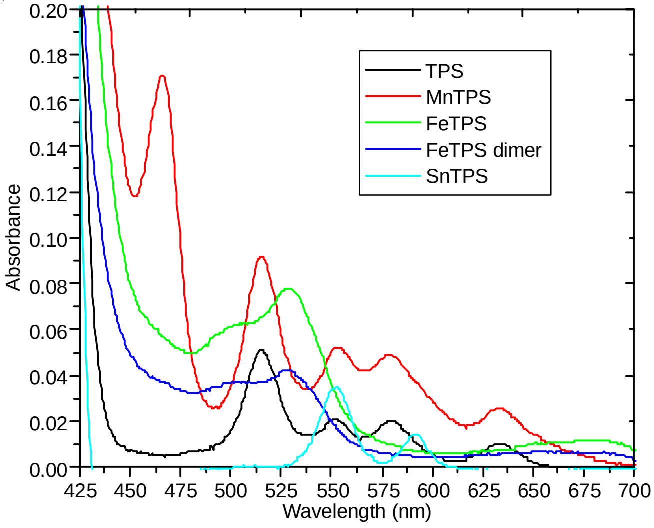

Fig. 1. Absorption bands of each porphyrin in visible region

FTIR studies: Some characteristic bands for aqueous porphyrins are recorded by FTIR spectroscopy, which confirm the substitution of SO_3Na groups at four *para*-positions in phenyl rings of porphyrin moiety. In $TPPS_4$, these bands are 1041, 1128 and 1184 cm^{-1} whereas for other porphyrins 1041 cm^{-1} is a common band, 1128 cm^{-1} is also nearly common and there is difference for 1184 cm^{-1} band. The other observed values for $MnTPPS_4Cl$, $FeTPPS_4Cl$, $(FeTPPS_4)_2$-O, and $SnTPPS_4Cl_2$ are 1192, 1240-1175, 1188 and 1195 cm^{-1}, respectively [35-37] (Table-2). Further, it should be emphasized that the monomer $FeTPPS_4Cl$ and a dimer $(FeTPPS_4)_2$-O are differentiated from each other by 850 and 881 cm^{-1} bands due to Fe-O-Fe stretching in dimer [36,37], where IR absorption bands are shown from 1150 -100 cm^{-1}, respectively (Fig. 2).

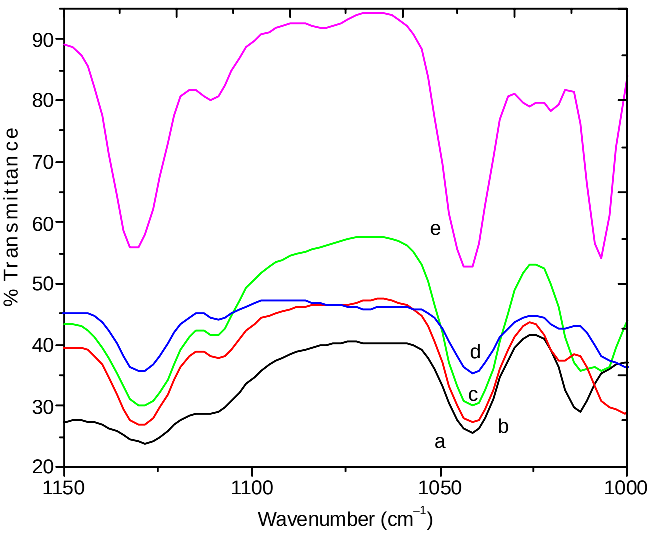

Fig. 2. Overlay of IR spectra for (a) $TPPS_4$, (b) $FeTPPS_4Cl$, (c) $MnPPS_4Cl$, (d) $(FeTPPS_4)_2$-O and (e) $SnTPPS_4Cl_2$ for their characteristic bands

^{1}H NMR studies: It is observed (Fig. 3) that in $TPPS_4$ as compared to pyrrole protons, *ortho*-phenyl protons are shifted to more down-field value *i.e.* 8.53 δ ppm (*o*-phenyl), 7.38-7.4 δ ppm (*m*-phenyl) and 8.05-8.03 δ ppm (β-pyrrole protons). In case of $MnTPPS_4Cl$ as shown in Fig, 4, it is observed that 8.51 δ ppm (*o*-phenyl), 7.5 δ ppm (*m*-phenyl) and 8.07 δ ppm (β-pyrrole protons). Similarly, even though $MnTPPS_4Cl$ is paramagnetic in nature, due to the presence of axial Cl ligand, the proton shifts are again seen at the position of diamagnetic porphyrins [35].

Diffused reflectance spectroscopic (DRS) studies: DRS spectra of aqueous-porphyrins was recorded to calculate the band-gap energy (eV) in the series of synthesized porphyrins. In present case, the suitable wavelength was 300-800 nm, where

TABLE-2
INFRARED SPECTRA, BAND GAP ENERGIES AND FLUORESCENCE INTENSITIES OF BASE-FREE AND METALLOPORPHYRINS

Porphyrin	Absorption bands (cm^{-1})			Band gap energy (eV)	Fluorescence intensity	Magnetic moment μ_{eff} (B.M.)
$TPPS_4$	1184 (s)	1128 (s)	1041(s)	1.66	448.06	–
$MnTPPS_4Cl$	1192 (s)	1128 (s)	1041 (s)	1.68	349.28	1.82
$FeTPPS_4Cl$	1175-1240 (s)	1130 (s)	1041 (s)	1.75	6.03	1.56
$(FeTPPS_4)_2$-O	1188 (s)	1128	1041 (m)	1.73	10.03	1.62
$SnTPPS_4Cl_2$	1195 (s)	1130 (s)	1041 (s)	1.75	367.38	–

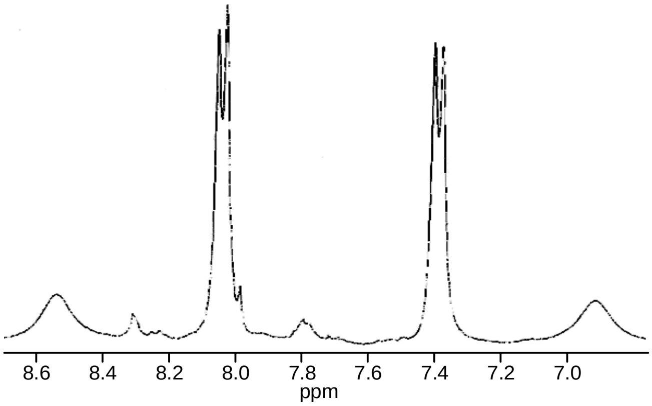

Fig. 3. Proton NMR spectra of TPPS$_4$

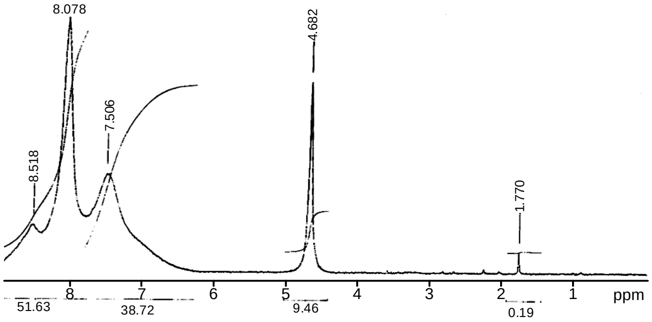

Fig. 4. Proton NMR spectra of MnTPPS$_4$Cl

BaSO$_4$ was used as a reference material. It a non-destructive technique, used for semiconductors such as above synthesized porphyrins. Table-2 shows the respective values of band-gap energies, which range between 1.66-1.75 eV, which make them the powerful photocatalysts. Fig. 5 shows the DRS spectra of FeTPPS$_4$Cl and (FeTPPS$_4$)$_2$-O as representative porphyrins.

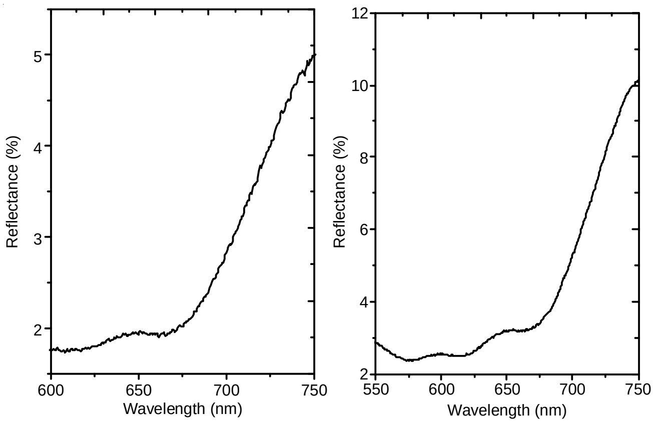

Fig. 5. DRS spectra of FeTPPS$_4$Cl and (FeTPPS$_4$)$_2$-O

Elemental analysis: As an example, MnTPPS$_4$Cl, was subjected for elemental analyzer to analyze of C, H, N where, following results were obtained as calcd. (found)%: C, 39.76 (38.61), H, 4.22 (4.28) and N, 3.65 (3.62).

Fluorescence studies: It is an accepted fact that most of the luminescence and photochemistry observed from porphyrins is associated with π-π^* states of porphyrin ring, even though, the lifetimes and reactivity of these states depend strongly on the metal ion incorporated in the porphyrin moiety [38]. When metals are containing either empty or full *d*-orbitals, form complexes which fluoresce at room temperature [39]. In the above series, TPPS$_4$ has no metal, therefore, fluoresce, SnTPPS$_4$Cl$_2$ has full *d*-orbitals hence it fluoresces, while in MnTPPS$_4$Cl the oxidation state of Mn is +3, where fluorescence is also observed. Thus, fluorescence is a characteristic property of some of the porphyrins, which can be also viewed for the role of fluorescent substances in photodegradation studies of rhodamine B dye. The results of fluorescence intensity are shown in Table-2. The overlay of fluorescence intensity of only fluorescent porphyrins is shown in Fig. 6.

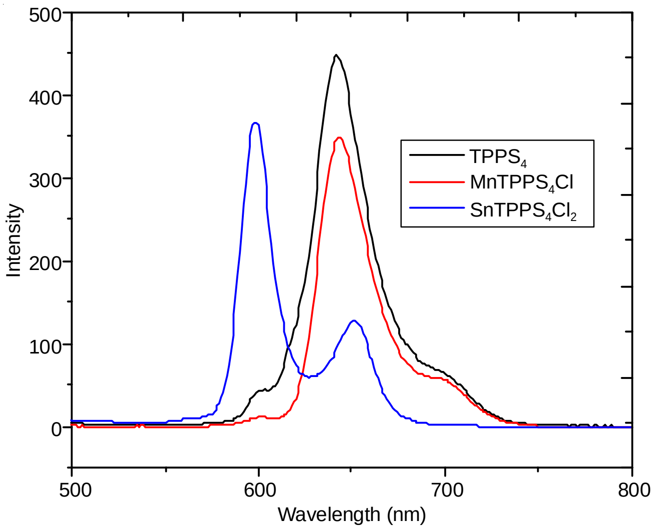

Fig. 6. Fluorescence spectra of porphyrins

Magnetic moment: To study the effect of diamagnetic and paramagnetic porphyrins, on the photodegradation studies of rhodamine B dye, the magnetic measurements of above porphyrins were carried out for the magnetic susceptibility, magnetic moment and subsequently the number of unpaired electrons, It was observed that TPPS$_4$ and SnTPPS$_4$Cl$_2$ were found diamagnetic whereas others MnTPPS$_4$Cl, FeTPPS$_4$Cl and FeTPPS$_4$)$_2$-O were found as low spin paramagnetic chelates (Table-2).

Photodegradation process: Several research works are focussed for dye degradation process by means of heterogeneous catalysis, where, after the process, the photocatalysts are fully recovered and sludge formed due to photocatalysis is minimum or negligible [40]. In this process, there is a direct attack on the chromophoric groups of the organic dyes or other organic impurities and thereby the reaction is boosted towards degradation [41]. Generally, the requirement of UV or visible radiation for the degradation process and the products found after degradation process depend upon the nature of the catalyst used. In present study, the medium chosen was acetone because it can easily mixed with polar as well as non-polar solvents. The series of synthesized porphyrin photocatalysts was TPPS$_4$, MnTPPS$_4$Cl, FeTPPS$_4$Cl, (FeTPPS4)$_2$-O and SnTPPS4Cl$_2$. These are deliquescent in nature (highly water soluble) but insoluble in acetone. The factors affecting the process of degradation are, amount of catalyst, saturation of reaction mixture with or without O$_2$, time and period of solar radiation.

Optimization of amount of catalyst: By varying the amount of porphyrins as photocatalysts in a systematic way for a solution of rhodamine B dye of 10^{-5} M concentration, an optimum amount of photocatalyst was confirmed. For this, the amounts such as 5,10, 15, 20, 25 and 30 mg were used to check the effectiveness of the photocatalysts. It was observed that 5 mg of catalyst was sufficient for 50 mL of 10^{-5} M solution of rhodamine B dye. However, when the amount was exceeded 5 mg, it was observed that the process of degradation was immeasurably fast, where no measurement with spectrophotometer was possible. Thus, 5 mg of photocatalyst was confirmed for the photocatalytic reaction. It was also observed that for a degradation process, the other factors *i.e.* saturation with O_2, addition of any suitable oxidizing agent, any promotors were not required. It is to be emphasized that after keeping the reaction assembly at 11.30 a.m., the process of degradation of dye took the time range of 25 to 40 min depending up on the type of porphyrin used.

Photodegradation of rhodamine B dye: A rhodamine B dye solution (10^{-5} M) was subjected to photocatalysis in acetone medium and solar radiation were induced in a reactor for further reaction. It was observed that $TPPS_4$ and a dimer of iron $(FeTPPS_4)_2$-O degraded the dye to 100% within 25 min. The remaining photocatalysts such as monomer of Fe *i.e.*, $FeTPPS_4Cl$ took 30 min, $MnTPPS_4Cl$ required 35 min and $SnTPPS_4Cl_2$ degraded the dye within 40 min. Fig. 7 shows the photodegradation pattern of Rhodamine B by all photocatalysts while Fig. 8 shows the degradation pattern of individual $TPPS_4$. The important observation to be noted in this regard is, in this process of heterogeneous catalysis, the generation of free hydroxyl ions (•OH) would be rapid enough to degrade the dye very effectively within a short time. Even though the photocatalysts porphyrins show slightly variation individually in degradation time, but that difference is very negligible. Thus, all these porphyrins are very effective photocatalysts. When some of photocatalysts as examples were recycled, it was found that their efficiency remains same up to five cycles. After each recycle, they were subjected to UV-vis and IR analysis for the verification of the change in their molecular structure. It was found that there is no change in the structure of respective photocatalysts after their reuse.

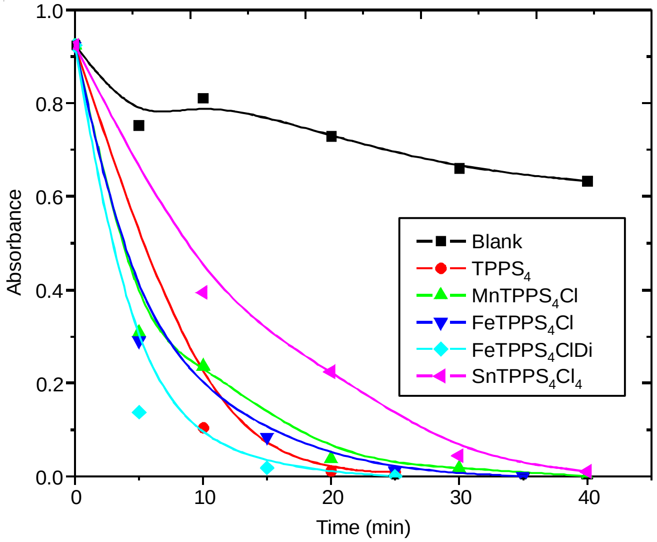

Fig. 7. Photodegradation pattern of rhodamine B

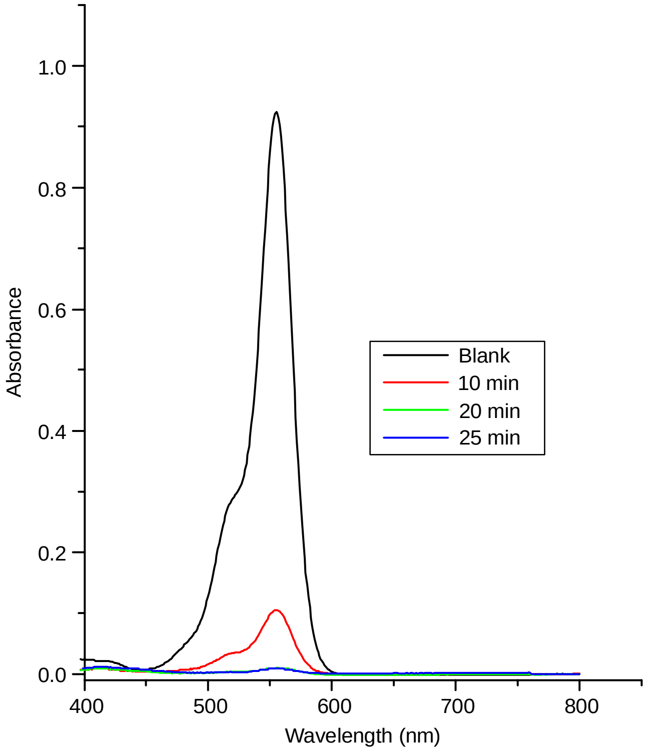

Fig. 8. Photodegradation of rhodamine B by $TPPS_4$

HPLC studies: The HPLC analysis of the studied dye has shown that the retention times for undegraded and degraded dye were 3.23 and 4.28 min. The respective peak area and peak height of the degraded and undegraded dye are shown in Table-3, where it is observed that degraded dye has larger peak area and larger peak height by 83,729 μV sec and 1,04,031 μV. It is revealed that the components are different before and after degradation.

Ion chromatography studies: In case of ion chromatography the cation column was calibrated for presence of Na^+ and NH_4^+ and anion column was calibrated for presence of Cl^-, SO_4^{2-}, NO_3^- and NO_2^-, respectively. Further, when undegraded and degraded dye solutions were analyzed by ion-chromatography, it was observed that amount of 0.15 μg of NH_4^+ and 1.80 μg of Cl^- per mL of dye solution were observed. This supports to the fact that complete degradation of the dye with mineralization. Figs. 9-11 show the ion-chromatograms for

TABLE-3
HPLC RESULTS OF RHODAMINE B

Dye	Retention time (min)	Area (μV s)	Height (μV)	Temperature
Rhodamine B (undegraded)	3.23	984312.19	126135.62	Ambient
Rhodamine B (degraded)	4.28	1068041.38	230166.82	Ambient

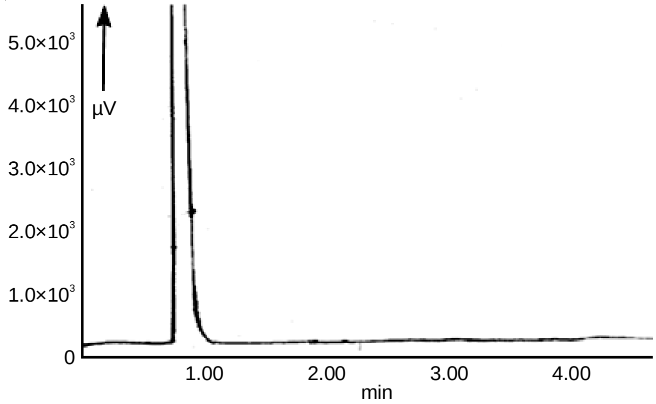

Fig. 9. Ion-chromatogram for undegraded rhodamine B

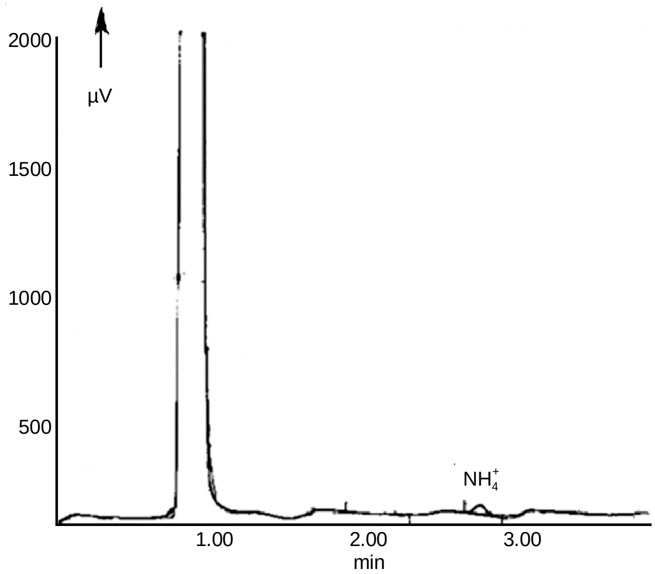

Fig. 10. Ion-chromatogram for degraded rhodamine B when calibrated for cations

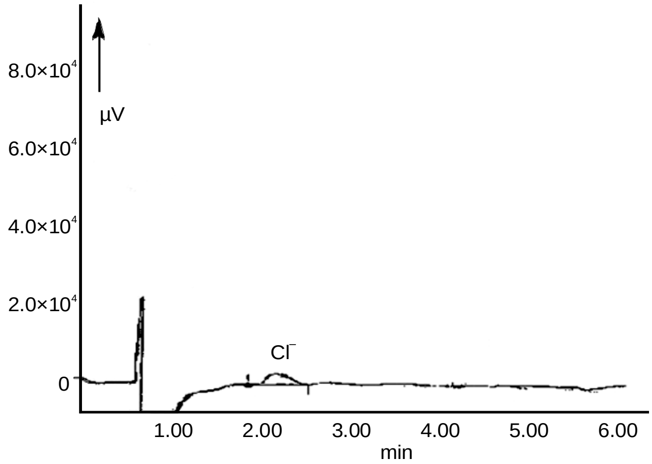

Fig. 11. Ion-chromatogram for degraded rhodamine B when calibrated for anions

undegraded and degraded dye for cations and anions. In chromatogram for undegraded dye, no peaks of any kind are observed whereas in the degraded dye for cation, presence of NH_4^+ and in degraded dye chromatogram for anions only Cl^- ions are observed. Thus, ion-chromatography has given the insight for the rupture of chromophoric groups in rhodamine B dye.

In the context of above porphyrins, the magnetic measurements of these photocatalysts have shown that $TPPS_4$ and $SnTPPS_4Cl_2$ are diamagnetic whereas $FeTPPS_4Cl$, $(FeTPPS_4)_2$-O and $MnTPPS_4Cl$ are paramagnetic in nature. However, photocatalytic activity is very good for $TPPS_4$ and $(FeTPPS_4)_2$-O and slightly less in case of $FeTPPS_4Cl$, $MnTPPS_4Cl$ followed by $SnTPPS_4Cl_2$. This confirms the following decreasing order of photocatalysis for the studied porphyrins: $TPPS_4$ > $(FeTPPS_4)_2$-O > $FeTPPS_4Cl$ > $MnTPPS_4Cl$ > $SnTPPS_4Cl_2$.

Thus, photocatalytic activity is seen to be independent of the number of unpaired or paired electrons in a given chelate. Secondly, the fluorescence intensity values (Table-2) show that $TPPS_4$, $MnTPPS_4Cl$ and $SnTPPS_4Cl_2$ are fluorescent whereas $FeTPPS_4Cl$ and $(FeTPPS_4)_2$-O are non-fluorescent. But the catalytic activity cannot be corelated with the fluorescence intensity since TPPS4 (fluorescent) and $(FeTPPS_4)_2$-O and $FeTPPS_4Cl$ (non-fluorescent) are the very good photocatalysts. Therefore, the property of fluorescence is also independent of the catalytic activity.

Conclusion

The synthesis and characterization of aqueous free-base porphyrin and metalloporphyrins such as $TPPS_4$, $(FeTPPS_4)_2$-O, $FeTPPS_4Cl$, $MnTPPS_4Cl$ and $SnTPPS_4Cl_2$ was carried out for the photodegradation of rhodamine B dye in acetone medium. Before the photocatalytic reaction their thermal stability was also investigated and found that all of them are stable up to 360 ºC, thus, safe to be used as photocatalysts. The sulphonated aqueous-porphyrins are used for various applications but their photocatalytic activity in case of trivalent and tetravalent metal ions was verified first time in the photodegradation of rhodamine B dye by synthesized porphyrins. The order of photocatalytic activity was observed as: $TPPS_4$ > $(FeTPPS_4)_2$-O > $FeTPPS_4Cl$ > $MnTPPS_4Cl$ > $SnTPPS_4Cl_2$. The complete degradation and mineralization within 25 -40 min revealed that the practical applications of these porphyrins as effective photocatalysts may be exploited in the respective industries. It is also observed that the magnetic properties such as diamagnetic or paramagnetic properties of porphyrin chelates and their fluorescence intensities have no corelation with the efficiency of the photocatalytic activity.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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