



## Photodegradation of Rhodamine B using Aqueous Free-Base Porphyrin and Metalloporphyrins of Divalent Metal Ions

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The present study is focused on the photodegradation of rhodamine B using aqueous free-base photocatalysts in presence of solar radiation. All catalysts such as free-base tetrasodium *meso*-tetra(*p*-sulphonatophenyl)porphyrin (TPPS<sub>4</sub>) or abbreviated as TPS and substituting M = Co, Ni, Cu, Zn and Ag into the moiety of TPS to get metalloporphyrins, were synthesized. Further, they were characterized by UV-visible, IR and <sup>1</sup>H MMR spectroscopic techniques. The photodegradation of rhodamine B of concentration 10<sup>-5</sup> M was carried out with 5 mg of a photocatalyst of free-base and other metalloporphyrins. It was observed that these synthesized photocatalysts have shown the photodegradation efficiency to the extent of 100% within time period of 5 to 40 min. The process of degradation was verified with HPLC and ion-chromatography.

**Keywords:** Rhodamine B, Free-base porphyrin, Metalloporphyrins, Photodegradation.

### INTRODUCTION

Synthetic dyes are much more commonly used in the industrial and commercial applications due to their colour flexibility and improved lasting power after application. Due to the inefficiency of dyeing process, in the textile industries, up to 2,00,000 tons of these dyes are lost every year during dyeing and finishing operations. The textile industry consumes a substantial amount of water in its manufacturing processes used mainly in the dyeing and finishing operations of the plants. The wastewater from textile plants is classified as the most polluting of all the industrial sectors. The extensive use of dyes in textile industry and the high concentration of organic pollutants and high stability of modern synthetic dyes poses a serious problem for the quality of water and the concerned environment. The conventional biological methods for the treatment of the effluent are ineffective [1]. Various techniques have been employed for the treatment of organic molecules in dye water. The approach includes chemical, physical, biological and their combinations [2]. Some of these methods were not suitable in some cases. For example, the chemical methods employing activated carbon are very effective in removing the synthetic

dye. However, it is suitable for treating only small effluent volume. Besides, the operation requires a long time and high capital cost [3]. Physical methods like coagulation, flocculation and reverse osmosis were also implemented. The major drawback of these methods is the formation of secondary waste products. Biological treatments always need strict control on temperature and pH. The degradation of synthetic dye takes a long process and disposal of a large amount of sludge was a serious problem. However, it has been found that these conventional biological treatment methods are ineffective for synthetic dyes having recalcitrant nature [4,5]. In recent years, a broad range of synthetic dyes have been extensively studied to develop a more promising technology based on advanced oxidation process (AOPs) which has an ability to oxidize contaminants quickly and non-selectively [6-8].

Advanced oxidation processes (AOP), which are currently in use are of prime importance for the effective oxidation of a wide variety of organic pollutants and synthetic dyes [9,10]. Presently, ozone is one of the most widely used advanced oxidation processes. It has a high standard reduction potential of 2.07 V and it can oxidize most organic and inorganic compounds. Especially, it is known to be a powerful method to decolorize

reactive dyes by destroying the chromophoric groups. Thus, AOPs are based on the generation of reactive hydroxyl radicals which can oxidize a broad range of organic pollutants quickly and non-selectively [11,12]. AOPs emphasize photocatalysis systems such as combination of semiconductors and light/solar radiation, or semiconductors and oxidants. It is also observed and verified that heterogeneous photocatalysis has emerged as an important destructive technology leading to the rupture of bonds of the hydrocarbon rings of the dyes with complete mineralization [13,14].

Generally, for photodegradation, wide band gap semiconductors such as  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{CdS}$ ,  $\text{SnO}_2$ ,  $\text{ZrO}_2$ , *etc.* are used [15]. Many researchers use mercury lamp, fluorescent lamp and halogen lamp to degrade dyes [16-18]. Further, an attempt is made to use solar radiation, which is abundantly and freely available in the tropical countries such as India, to degrade the dyes [19-21]. The present objective of photodegradation of rhodamine B utilizes the self-synthesized aqueous porphyrins, which are narrow band gap semiconductors (1.66-1.83 eV). They are quite competitive as compared to the above-mentioned semiconductors where band gap ranges between (3.2-3.9) [22].

Previously, the efforts have been done by using the non-aqueous porphyrins coatings on the above-mentioned inorganic semiconductors. But, in present study, an exclusive aqueous-porphyrins are used only without any other semiconductors. Simultaneously, no oxidizing agents such as  $\text{O}_2$ ,  $\text{H}_2\text{O}_2$  or  $\text{K}_2\text{S}_2\text{O}_8$  were used in a reaction assembly to verify the efficiency of selected photocatalysts. Before, the use of these photocatalysts, their thermal stability was confirmed that they are quite stable up to  $400^\circ\text{C}$  and can be safely used for photodegradation reaction [23]. The importance of these aqueous porphyrins has been revealed by the exhibition of their excellent antiviral activity against the human immunodeficiency virus [24]. They are also widely used in the clinical experiments as potential sensitizers in photosensitized tumor therapy (PTT) and as colourant stabilizers in ink jet printers [25-27]. Here before, exclusively non-aqueous porphyrins were effectively used to carry out photodegradation of amido black 10B and methyl orange in aqueous-medium [28,29].

Rhodamine B, a brightly coloured synthetic pigment has been extensively used as a dye in many industries, including those that produce paper, paints, textiles, leather and porcelain. Long-term contact with rhodamine B may cause cancer and birth defects; thus, it has been prohibited as a food additive [30,31]. The addition of rhodamine B to cosmetics also may be linked to the potential threat of cancer and birth defects in humans, thereby creating the need to establish efficient methods for its sensitive and rapid determination in cosmetics [32].

## EXPERIMENTAL

The free-base tetra sodium *meso*-tetra(*p*-sulphonato phenyl)porphyrin (TPPS<sub>4</sub>) was synthesized by standard method [33]. Finely ground pure TPP (0.003 mol) and conc.  $\text{H}_2\text{SO}_4$  (0.5 mol) were refluxed in a two-necked flask for 8 h and the reaction mixture was kept aside for 48 h without any disturbance. The entire reaction was further diluted with distilled

water, then heated and lime (CaO) was added until the solution acquires purple colour. The solution was filtered to remove  $\text{CaSO}_4$ , washed with hot water and the filtrate was concentrated to small volume (150-200 mL). The conc.  $\text{Na}_2\text{CO}_3$  solution was added and the pH of the solution was adjusted to 8-10. The precipitated  $\text{CaCO}_3$  was removed by filtration and 90%  $\text{C}_2\text{H}_5\text{OH}$  was added periodically. The filtrate was concentrated on steam bath and further dried in oven at  $100^\circ\text{C}$  for 2 h. At this stage, TPPS<sub>4</sub> crystals were collected and preserved in air tight capsule. The purification of TPPS<sub>4</sub> was carried out by using dry-column chromatography on basic alumina column, which acts as a stationary phase. The mobile phase prepared for gradient elution was comprised of water, methanol and acetone in the ratio 7:2:1 [33]. During elution, only purple coloured fraction due to TPPS<sub>4</sub> was collected and other fractions were rejected.

The above purified TPPS<sub>4</sub> was used to synthesize aqueous-metalloporphyrins. The divalent metals used were Co, Ni, Cu, Zn and Ag, respectively. The metalloporphyrins, such as  $\text{CoTPPS}_4$ ,  $\text{NiTPPS}_4$ ,  $\text{CuTPPS}_4$ ,  $\text{ZnTPPS}_4$  and  $\text{AgTPPS}_4$  were synthesized by taking respective metal salt in ethanol and TPPS<sub>4</sub> in stoichiometric proportions and refluxing the solution on steam bath for 0.5 h. The purification of these porphyrins was done using dry-column chromatography as described above. There were three types bands on the column *viz.* blood red colour due to respective metalloporphyrin, green colour due to dication and colourless band due to unreacted metal salt. From these bands, only blood red coloured band was selected, tested with TLC and completion of reaction was confirmed by spectrophotometry. The yield of purified porphyrin was in the range of 80-85%.

**Characterization:** UV-visible spectra were recorded on Shimadzu spectrophotometer (model UV/2450UV) using  $10^{-4}$  M and  $10^{-5}$  M concentrations for each porphyrin. IR analysis of solid porphyrins was carried out using Shimadzu IR spectrometer (model Prestige/21FTIR). <sup>1</sup>H NMR spectra were recorded using Varian 300 MHz model. Diffused reflectance spectroscopy (DRS) was performed to calculate band gap energies on Shimadzu UV-visible spectrophotometer (model UV/2450 UV).

**Photodegradation of rhodamine B:** Solar assisted photocatalytic degradation of rhodamine B, which is a xanthen dye, was carried out in acetone medium. The AR grade acetone was refluxed with  $\text{KMnO}_4$  for 2 h till pink colour persists and distilled to get the solvent of desired purity. The  $10^{-5}$  M concentration solution of dye was used in acetone medium and a process of degradation was carried out at the regular interval of 5 min. The degraded reaction mixture was subjected to HPLC using Perkin-Elmer SERIES-200 with C18 column of dimensions 250 mm × 4.6 mm and particle size 5 μm. The solvent system selected was methanol and water 80:20% with UV-visible detector. Further, ion chromatography was used on Shodex-CDS 5 analyzer to verify the mineralization of the dye (rhodamine B).

## RESULTS AND DISCUSSION

**UV-visible studies:** The porphyrins TPPS<sub>4</sub>,  $\text{CoTPPS}_4$ ,  $\text{NiTPPS}_4$ ,  $\text{CuTPPS}_4$ ,  $\text{ZnTPPS}_4$  and  $\text{AgTPPS}_4$  were characterized by UV-visible spectroscopy. The sorbet band is a characteristic

absorption band for a respective porphyrin. The absorption bands appearing for all these compounds in solet and visible region are in good agreement with the literature values as shown in Table-1. It can be observed that solet band ranges in between 413 to 425 nm, whereas other characteristic bands (Q bands) vary from 525 to 552 nm. Only in case of TPPS<sub>4</sub>, the four bands obtained at 516, 552, 579 and 633 nm. When respective metal ions are substituted in the free-base porphyrin ring, the characteristic bands for above porphyrins observed are 540, 525, 539, 556 and 540 nm with the disappearance of other three bands as are observed in TPPS<sub>4</sub>. This confirms the formation of metalloporphyrins for corresponding metals as is shown in Figs. 1 and 2. In Fig. 1, as an example, the UV-visible spectra of ZnTPPS<sub>4</sub> for 10<sup>-4</sup> M and 10<sup>-5</sup> M concentrations are shown and in Fig. 2 characteristic absorption bands for all porphyrins are shown.

Porphyrin	Absorption bands				
	Soret band	← Q-bands →			
TPPS <sub>4</sub>	413	516	552	579	633
CoTPPS <sub>4</sub>	425	–	540	–	–
NiTPPS <sub>4</sub>	409	–	525	–	–
CuTPPS <sub>4</sub>	412	–	539	–	–
ZnTPPS <sub>4</sub>	421	–	556	–	–
AgTPPS <sub>4</sub>	422	–	540	–	–

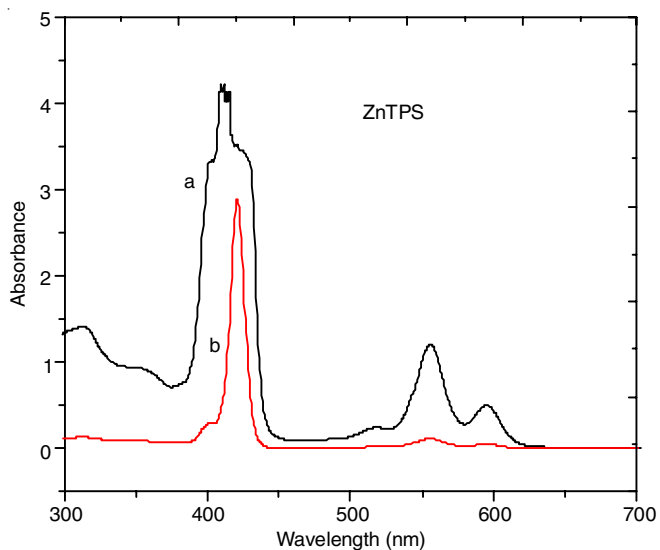


Fig. 1. UV-visible spectra of ZnTPPS<sub>4</sub> (a) 10<sup>-4</sup> M and (b) 10<sup>-5</sup> M concentration

**Infrared studies:** The characteristic absorption bands for aqueous-porphyrins are obtained when non-aqueous porphyrins are sulphonated with the substitution of -SO<sub>3</sub>Na groups. In case of TPPS<sub>4</sub>, due to N-H and O-H stretching frequency, the absorption bands in the region 3590-3440 cm<sup>-1</sup> are obtained. But when metal ions are substituted in porphyrin moiety, even though N-H band disappears, due to O-H stretching frequency the band in the vicinity of N-H frequency is obtained. The absorption bands for the confirmation of sulphonation are 1184(s), 1128(s) and 1041(s) cm<sup>-1</sup> whereas for other metallo-

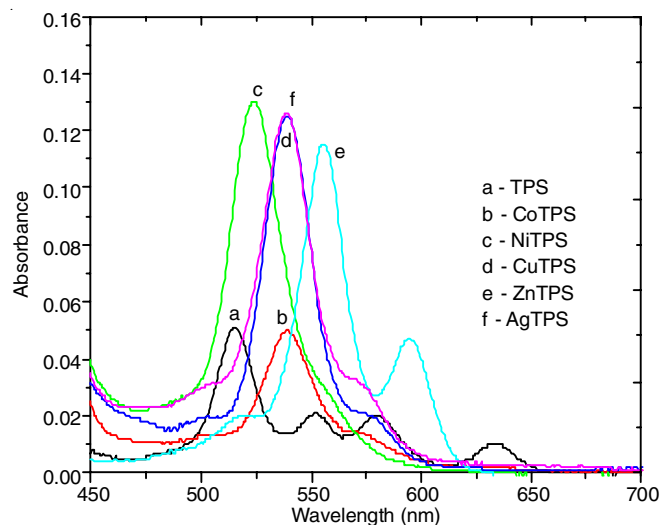


Fig. 2. Characteristic band of each porphyrin in visible region

porphyrins, there is increase in the values for absorption bands, which was confirmed earlier [34,35]. The respective values for absorption bands and the values of band gap energies are shown in Table-2 and overlay of absorption bands is shown in Fig. 3.

Porphyrin	Absorption bands (cm <sup>-1</sup> )			Band gap (eV)
TPPS <sub>4</sub>	1184 (s)	1128 (s)	1041 (s)	1.66
CoTPPS <sub>4</sub>	1199 (m)	1130 (m)	1043 (m)	1.76
NiTPPS <sub>4</sub>	1188 (s)	1128 (s)	1039 (s)	1.83
CuTPPS <sub>4</sub>	1184 (s)	1130 (s)	1041 (s)	1.79
ZnTPPS <sub>4</sub>	1193 (s)	1128 (s)	1041 (s)	–
AgTPPS <sub>4</sub>	1186 (s)	1130 (s)	1041 (s)	1.74

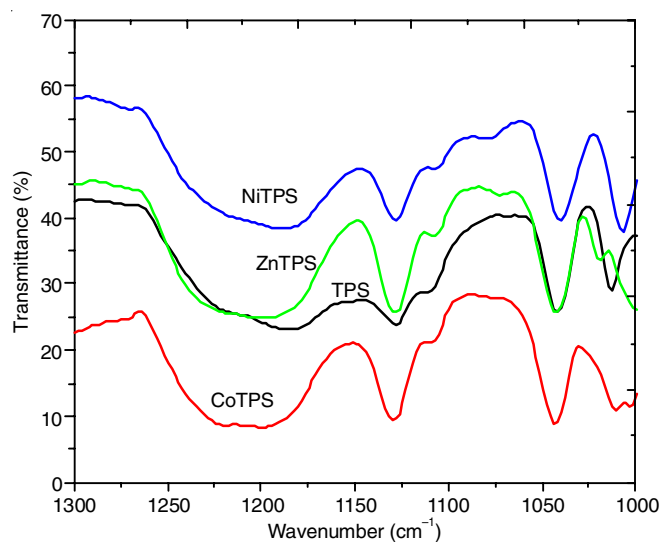


Fig. 3. Overlay of IR spectra for TPPS<sub>4</sub>, CoTPPS<sub>4</sub>, NiTPPS<sub>4</sub> and ZnTPPS<sub>4</sub> for their characteristic bands

**NMR studies:** The proton NMR spectra were recorded at 29 °C and chemical shifts are mentioned in δ ppm with reference to (CH<sub>3</sub>)<sub>4</sub>Si in deuterated chloroform (CDCl<sub>3</sub>). In

aqueous porphyrins like TPPS<sub>4</sub>, it is seen that *ortho*-phenyl protons are shifted to more down-field value as compared to pyrrole proton signal. The reason may be due to the presence of SO<sub>3</sub>Na group at *para*-position of the phenyl ring, *ortho* protons may be deshielded. Therefore, in aqueous porphyrins *o*-phenyl protons have maximum downfield signal than β protons. In TPPS<sub>4</sub>, the values of *o*-phenyl, *m*-phenyl and β-pyrrole protons are 8.53, 7.38-7.4 and 8.03-8.05 ppm, respectively. In CoTPPS<sub>4</sub> (Fig. 4), which is paramagnetic in nature, *o*-phenyl protons are still more shifted to down-field as compared to TPPS<sub>4</sub>. The values for CoTPPS<sub>4</sub>, for *o*-phenyl, *m*-phenyl and β-pyrrole protons are 9.2, 8.06 and 8.9 ppm, respectively. These values are in good agreement with the literature values [35].

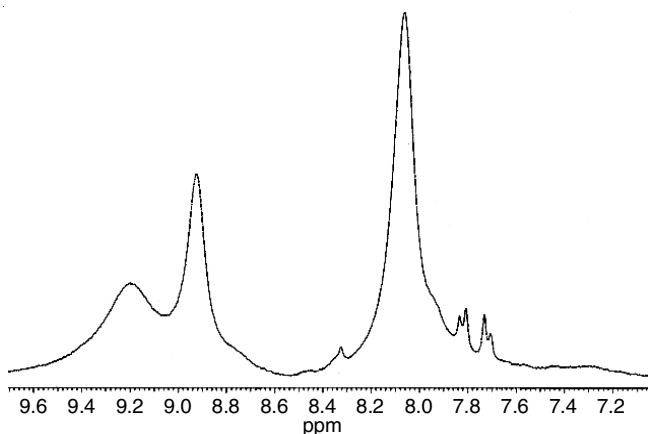


Fig. 4. Proton NMR spectra of CoTPPS<sub>4</sub>

**Diffuse reflectance spectroscopic studies:** Diffuse reflectance spectra of aqueous-porphyrins were recorded using wavelength range from 300 to 800 nm and BaSO<sub>4</sub> as a reference material. Reflectance data are usually expressed in terms of percent reflectance (%R), which is analogous to percent transmission in absorption spectroscopy. It is a non-destructive technique and used to determine the band gap energies in semiconductors such as above-mentioned porphyrins. Table-2 represents the band-gap energies in eV for selected free-base and other metalloporphyrins. Fig. 5 shows the DRS spectra of CuTPPS<sub>4</sub> and AgTPPS<sub>4</sub> as some of the examples in a given series of porphyrins. It is observed that the band gap energies range from 1.66-1.83 eV, which reveals that all of them are low band gap metal-organic semiconductors. Thus, this remarkable property of the porphyrins was used to carry out photodegradation of rhodamine B dye.

**Photodegradation process:** Some of the conventional methods used are precipitation, adsorption, flocculation, flotation, oxidation, reduction, electrochemical, aerobic, anaerobic and biological treatment methods. These methods have inherent limitations in technologies such as less efficiency and production of secondary sludge, the disposal of which is an expensive affair. Merely, transferring hazardous materials from one medium to another is not a long-term solution to the issue of toxic waste loading on the environment. Chemical coagulations for dye removal require loading of chemical coagulation and optimal operating conditions like pH and coagulation dosage should be rigidly reminded for achieving maximum dye removal. The coagulation-flocculation process can be utilized as a pre- or

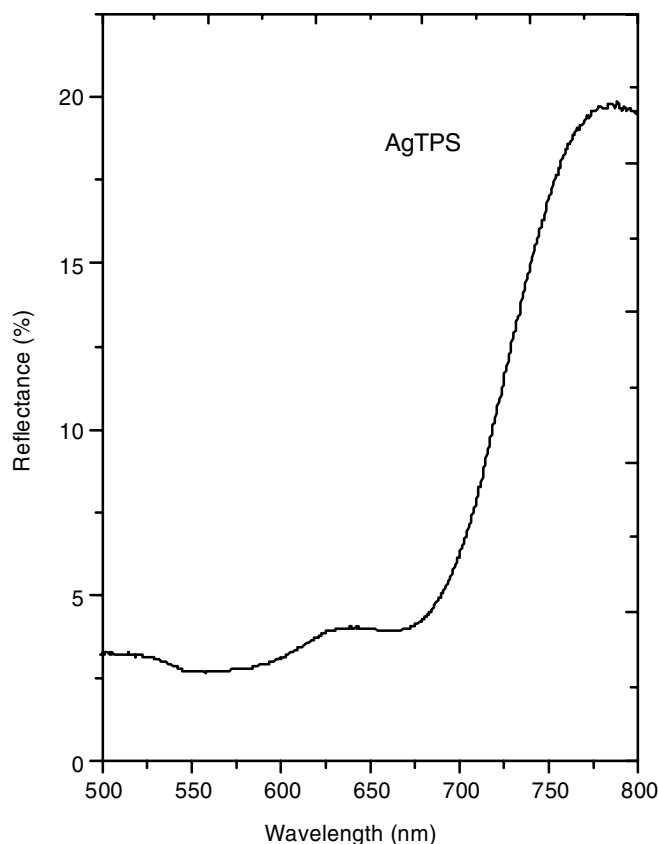
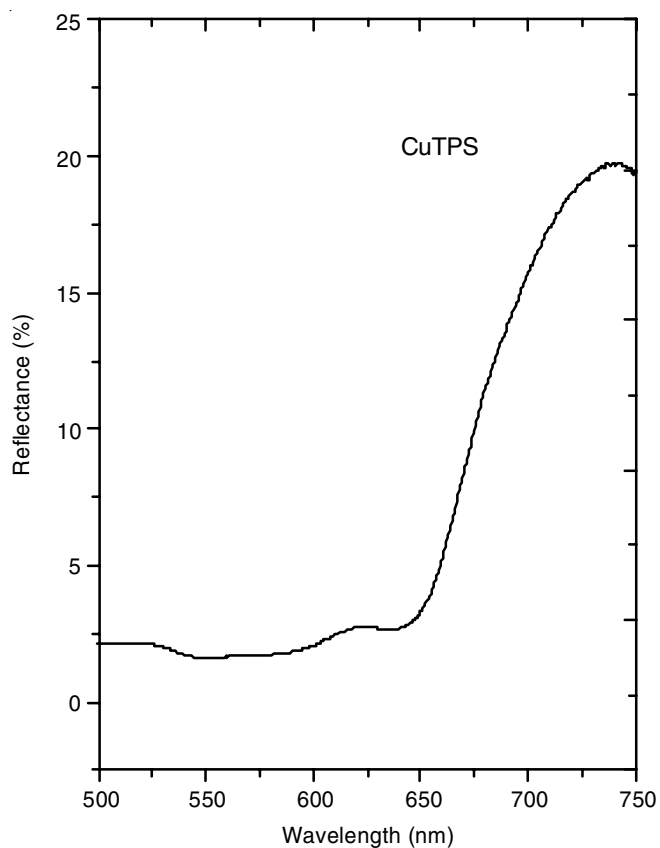


Fig. 5. DRS spectra of CuTPPS<sub>4</sub> and AgTPPS<sub>4</sub>

post- or even as a main treatment. This process is cost effective and easy as it consumes less energy than the conventional coagulation treatment [36]. However, using inorganic salts like aluminum chloride and aluminum sulfate as the coagulation agent has now become controversial because of their possibility of contributing to Alzheimer's disease [37,38]. Polyacrylamide based materials are also often utilized in the coagulation process, but the possible release of monomers is now considered damaging due to their entering into the food chain and causing potential health impacts (*e.g.* carcinogenic effects). The heterogenous photocatalyst relates to the water decontamination processes which are concerned with the oxidation of bio-recalcitrant organic compounds. This impressive method relies on the formation of highly reactive chemical species that degrade a number of recalcitrant molecules into biodegradable compounds and is known as advanced oxidation process (AOP).

Heterogeneous photocatalysis has proved to be as an efficient tool for degrading both atmospheric and aquatic organic contaminants [39]. It uses the sunlight in the presence of a semiconductor photocatalyst to accelerate the remediation of environmental contaminants and destruction of highly toxic molecules [40,41]. The type of the radiation used depends on the type of catalyst. Photodegradation of rhodamine B was carried out using hygroscopic powders of TPPS<sub>4</sub>, CoTPPS<sub>4</sub>, NiTPPS<sub>4</sub>, CuTPPS<sub>4</sub>, ZnTPPS<sub>4</sub> and AgTPPS<sub>4</sub>, which are highly soluble in aqueous medium but insoluble in acetone medium. Thus, these porphyrins were used to carry out the heterogeneous catalysis in a glass reactor in the presence of solar radiation. Rhodamine B is found to have  $\lambda_{\max} = 555$  nm in the acetone medium. For this degradation process, the optimum conditions such as absence of catalyst, presence of catalyst, the amount of catalyst, saturating reaction mixture with O<sub>2</sub> and without O<sub>2</sub>, time of irradiation, use of surfactant promoters. This was necessary to measure the efficiency of activity for degradation or removal of dye solution at different time intervals.

**Amount of catalyst and reaction assembly:** The optimum amount for photocatalyst was determined by varying the amount of porphyrins in 50 mL of 10<sup>-5</sup> M dye solution in a 150 mL capacity conical flask. The amount of photocatalyst was tested with 5, 10, 15, 20, 25 and 30 mg with the above dye solution at different intervals of time. It was observed that with 5 mg of porphyrins, the reaction was under control otherwise the degradation process with 10 mg and onwards was immeasurably fast. Therefore, 5 mg of each porphyrin was selected as an optimum amount for degradation of rhodamine B. The dye solution did not require saturation with O<sub>2</sub> or any surfactants or promoters. This was the special feature of these porphyrins in the photodegradation process. The reaction assembly was kept in the solar radiation at 11.30 am and observed that the degradation process was effective from 5 to 40 min, depending up on the nature of the respective porphyrin.

**Photodegradation of rhodamine B:** The synthesized aqueous porphyrins were used as photocatalysts for the degradation of rhodamine B in acetone medium. Further, it was observed that the entire process of degradation was completed within 40 min by all porphyrins, where a dye was degraded to the extent of 100%. This reveals the efficiency of synthesized

aqueous porphyrins. Fig. 6 shows that among all the porphyrins, CoTPPS<sub>4</sub> is degrading the dye within just 5 min whereas AgTPPS<sub>4</sub> degrades within 10 min. The other porphyrins such as NiTPPS<sub>4</sub>, TPPS<sub>4</sub> (free-base), CuTPPS<sub>4</sub> and ZnTPPS<sub>4</sub> require 20, 25, 40 and 40 min, respectively. The dye degradation pattern is shown in Fig. 7 for TPPS<sub>4</sub> and AgTPPS<sub>4</sub>, where complete degradation of rhodamine B is observed. It is also observed that among all the synthesized porphyrins even though all of them are efficient, CoTPPS<sub>4</sub> and AgTPPS<sub>4</sub> are highly efficient. The reason for this may be attributed to the fact that comparatively larger area and long-lived excited states of corresponding photocatalysts in the exhibition photocatalytic activity.

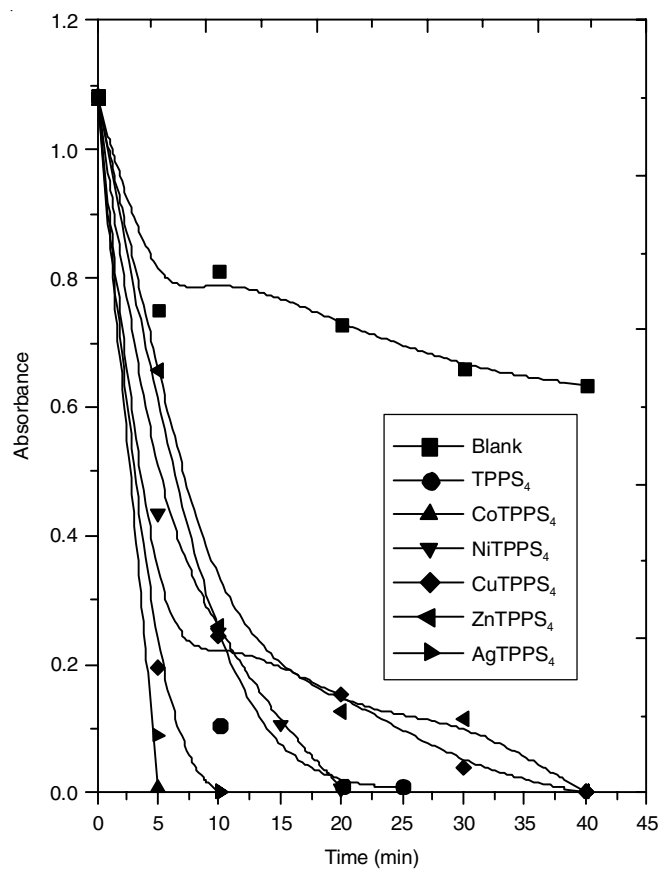


Fig. 6. Photodegradation of rhodamine B

Further, to check the reproducibility of the catalysts, recycling process of CoTPPS<sub>4</sub> as a representative porphyrin was carried out for six times is shown in Fig. 8. When it is observed meticulously, it reveals that for first three cycles CoTPPS<sub>4</sub>, the degradation process takes place within 5 min whereas for next three cycles it takes 10 min to complete 100% degradation. Thus, the reproducibility of the photocatalyst was verified and further, the chemical composition of CoTPPS<sub>4</sub> was confirmed by UV-visible and IR spectroscopies.

**HPLC analysis:** HPLC analyzer containing C-18 was used to know the number of components in the rhodamine B before and after degradation. It was further observed that undegraded dye when subjected to HPLC analysis, a single component with retention time (R.T.) 3.23 min was recorded. When the dye was degraded in presence of solar radiation,

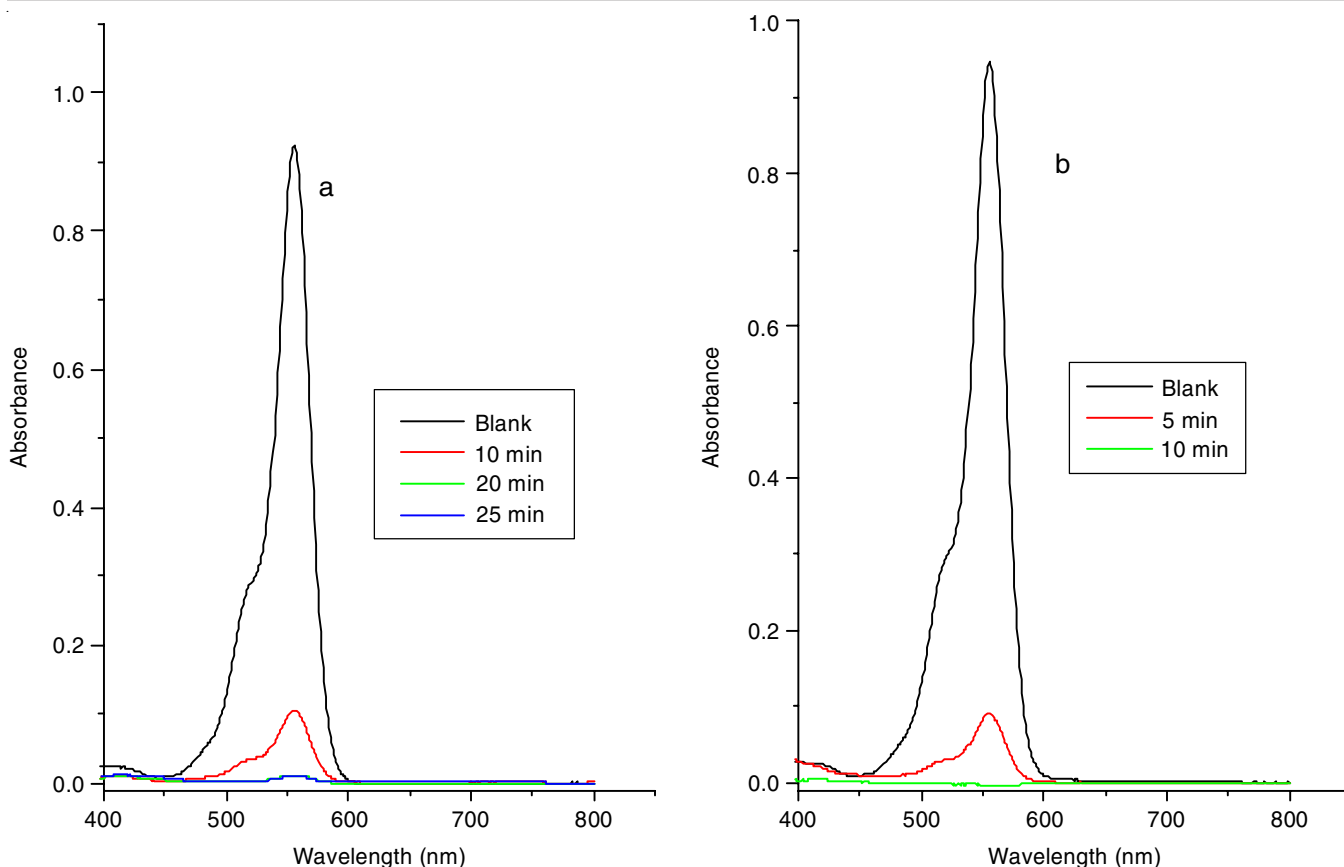


Fig. 7. Photodegradation of rhodamine B by (a) TPPS<sub>4</sub> and (b) AgTPPS<sub>4</sub>

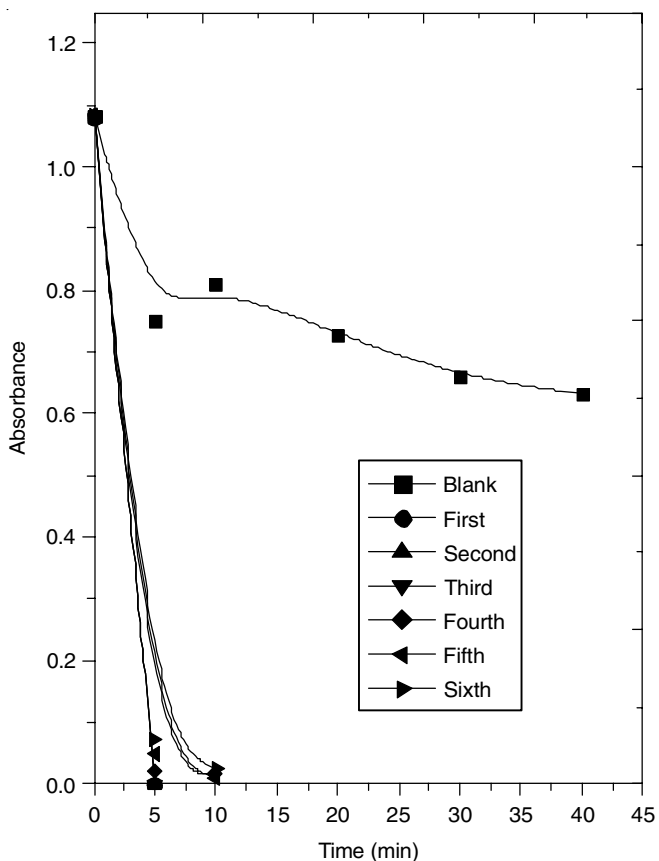


Fig. 8. Recycling of CoTPPS<sub>4</sub> for six times

which was then analyzed with HPLC, where, the component with retention time 4.28 min was observed. Thus, HPLC has shown that before and after the degradation process, even though, a single component was isolated, these were different with respect to their structures. Fig. 9 shows the HPLC chromatogram for degraded and undegraded rhodamine B.

**Ion-chromatography analysis:** The mineralization of dye after the process of degradation was confirmed by using ion-chromatography with Shodex-CD 5 analyzer. From the structure of rhodamine B, the cation analyzer was calibrated for the presence of NH<sub>4</sub><sup>+</sup> ions and anion analyzer was calibrated for Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> ions, respectively. Table-3 shows the presence of NH<sub>4</sub><sup>+</sup> and Cl<sup>-</sup> was detected whereas quantitative results show the concentration of ions (μg/mL), retention time (min), peak height (μV) and peak area (μV s). Thus, the amount of NH<sub>4</sub><sup>+</sup> and Cl<sup>-</sup>, quantitatively found was 0.15 and 1.80 μg/mL of the dye solution confirms the complete mineralization of rhodamine B dye. This observation also throws light on the reduction of =N(CH<sub>3</sub>)<sub>2</sub> and -N(CH<sub>3</sub>)<sub>2</sub> to NH<sub>4</sub><sup>+</sup> groups and finally giving NH<sub>4</sub><sup>+</sup> and Cl<sup>-</sup> ions in solution.

### Conclusion

The synthesis and characterization of aqueous-porphyrins such as TPPS<sub>4</sub>, CoTPPS<sub>4</sub>, NiTPPS<sub>4</sub>, CuTPPS<sub>4</sub>, ZnTPPS<sub>4</sub> and AgTPPS<sub>4</sub> was carried out for the photodegradation of rhodamine B dye in acetone medium. Since, the thermal stability of these porphyrins was up to 400 °C, these photocatalysts were safely used in the photodegradation process in solar radiation. Among

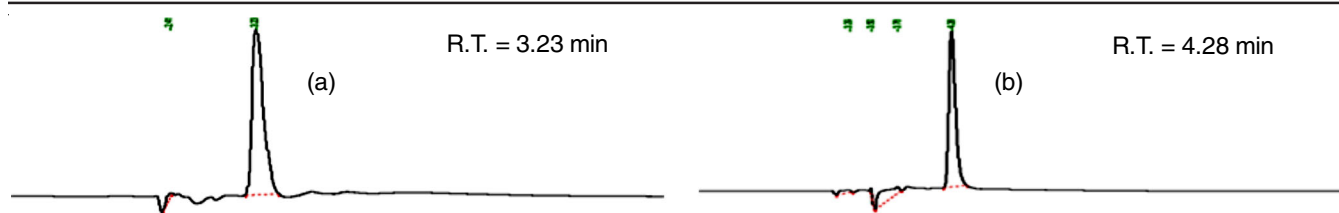


Fig. 9. HPLC chromatogram for rhodamine B (a) before degradation (b) after degradation

TABLE-3  
ION-CHROMATOGRAPHY RESULTS OF RHODAMINE B

Dye	Presence of cation/anion	Concentration ( $\mu\text{g/mL}$ )	Retention time (min)	Peak height ( $\mu\text{V}$ )	Peak area No. ( $\mu\text{V s}$ )
Rhodamine B (undegraded)	–	–	–	–	–
Rhodamine B (degraded)	$\text{NH}_4^+$	0.15	2.758	33.0	209.191
Rhodamine B (degraded)	$\text{Cl}^-$	1.80	2.342	2852.0	47279.000

all synthesized photocatalysts,  $\text{CoTPPS}_4$  and  $\text{AgTPPS}_4$  were found to degrade within 5 and 10 min whereas other porphyrins such as  $\text{NiTPPS}_4$ ,  $\text{TPPS}_4$ ,  $\text{CuTPPS}_4$  and  $\text{ZnTPPS}_4$  degrade the dye solution within 20, 25 and 40 min, respectively. The recycling of  $\text{CoTPPS}_4$  for six times has shown that first three recycling processes have degraded the dye within 5 min whereas for next three recycles 10 min were required. The recycling of the photocatalysts has shown that their activity remains nearly unchanged and there was no change in the chemical composition of the structure of the porphyrins, which was confirmed by UV-visible and IR spectroscopy. The HPLC analysis has given only one degraded component which is different from undegraded component which was certain on the basis of different retention times. The ion-chromatography analysis has shown the complete mineralization of the rhodamine B dye with the formation of  $\text{NH}_4^+$  and  $\text{Cl}^-$  ions.

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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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