



## Photodegradation of 1,5-dihydroxynaphthalene catalyzed by meso-tetra(4-sulfonatophenyl)porphyrin in aerated aqueous solution

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### ABSTRACT

The photodegradation of 1,5-dihydroxynaphthalene catalyzed by meso-tetra(4-sulfonatophenyl)porphyrin ( $H_2TPPS^{4-}$ ) under visible light irradiation in aerated aqueous solution has been studied and the main product has been identified as 5-hydroxy-1,4-naphthoquinone. It is found that the photodegradation is dependent on the pH of reaction system and the addition of sodium azide ( $NaN_3$ ) leads to a significant decrease in the degree of 1,5-dihydroxynaphthalene photodegradation. The species distribution of  $H_2TPPS^{4-}$  in solution was obtained from potentiometric titration experiments. It is suggested that the mono-protonated monomeric species  $[H(H_2TPPS)]^{3-}$  is the main active species of  $H_2TPPS^{4-}$  to catalyze 1,5-dihydroxynaphthalene photodegradation.

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### 1. Introduction

The quantity of phenolic compounds in surface and underground water have been increased dramatically in the last decades for their widespread application as the material of pesticides, herbicides and insecticides [1,2]. These compounds are well-known pollutants due to their slow degradation and high toxicity. Thus, efforts to develop new efficient methods to remove these compounds from wastewater become more and more important. Several methods for degrading phenolic compounds have been extensively investigated, such as microbial degradation [3–5], activated carbon adsorption [6–9], chemical oxidation [10,11], electrocatalytic oxidation [12,13], enzymatic polymerization using peroxidase enzymes [14–16] and photooxidation [17–20]. Among these methods, photooxidation using sensitizers and visible light appears to be particularly valuable.

Porphyrins and metalloporphyrins can efficiently harvest sunlight and have high molar absorption coefficients in the visible region, high quantum yields of photo-excited triplet states. Several free base porphyrins or metalloporphyrins have been reported to be

powerful sensitizers for the photooxidation of phenols and naphthols in organic solvent system [21–29]. Unfortunately, these porphyrins are insoluble in aqueous solution and difficult to use as sensitizers to remove phenolic compounds from wastewater. Thus, it is a topic of growing interest to photodegrade phenolic compounds using water-soluble porphyrin derivatives. Some water soluble sulfophenyl porphyrin derivatives, such as iron complex of meso-tetra(2,6-dichloro-3-sulfophenyl)porphyrin [30], meso-tetra(2,6-dichloro-3-chlorosulfophenyl)porphyrin and its tin and zinc complexes [27], have successfully used in the photodegradation of 4-chlorophenol and 2,6-dimethylphenol in aqueous solution.  $H_2TPPS^{4-}$ , meso-tetra(4-sulfonatophenyl)porphyrin, is known as a promising biomimetic catalyst possessing favorable photophysical properties that make it potentially applicable in the photodegradation of pollutants [24,25]. However, there are few reports focused on water-soluble sulfophenyl porphyrin derivatives used as sensitizers to degrade phenolic compounds. Pepe and his co-workers have reported that meso-tetra(4-sulfonatophenyl)porphyrin bound to aminopropyl silica and/or exchange resins displayed high photocatalytic effect [31]. In this work, we used  $H_2TPPS^{4-}$  as a photocatalyst to degrade 1,5-dihydroxynaphthalene under visible light irradiation in aerated aqueous solution. The effects of some reaction conditions, such as concentration of  $H_2TPPS^{4-}$ , pH and addition of  $NaN_3$ , on the photodegradation of 1,5-dihydroxynaphthalene were

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investigated. The species distribution of  $\text{H}_2\text{TPPS}^{4-}$  in solution was also investigated by potentiometric titration experiments and the active species of  $\text{H}_2\text{TPPS}^{4-}$  to degrade 1,5-dihydroxynaphthalene in the reaction system was suggested.

## 2. Experimental

### 2.1. Materials

$\text{H}_2\text{TPPS}^{4-}$  were synthesized by the method similar to [32]. 1,5-Dihydroxynaphthalene and  $\text{NaN}_3$  were obtained from Aldrich without further purification. Silica gel was obtained from Qingdao. Common organic reagents were of reagent grade and redistilled before use. The water used in all physical measurements was Milli-Q grade.

### 2.2. Instrumentation

Elemental analyses (C and H) were carried out by the PerkinElmer 240 elemental analyzer. Mass spectrometry analysis was performed on a Thermo LCQDECA-XP spectrometer. UV-vis spectra were recorded on Varian Cary 100 UV-Vis spectrophotometer.  $^1\text{H}$  NMR spectrum was recorded on a 300 MHz Bruker-AMX spectrophotometer. Potentiometric titration was performed on an automatic titrator (Metrohm 751GPD Titrino). For the photodegradation experiments of 1,5-dihydroxynaphthalene, a iodine tungsten lamp (300 W, Shanghai), ITL, was used.

### 2.3. Photodegradation experiments of 1,5-dihydroxynaphthalene

The photodegradation reactions of 1,5-dihydroxynaphthalene were carried out in a 20-ml jacketed reactor maintained at a certain temperature by circulation of thermostated water, with an oxygen atmosphere achieved by continuous bubbling of pure oxygen into the reaction mixture. A typical reaction mixture contained 0.2 M buffer (phosphoric/phosphate or acetic/acetate), 0.2 mM 1,5-dihydroxynaphthalene, 0.2 mM  $\text{H}_2\text{TPPS}^{4-}$  in a total volume of 15.0 ml were added into the reactor. After a few minutes of oxygen purging, the reactor was irradiated with an external ITL till the concentrations of reactant and products reach certain values. The progress of the reaction was monitored by UV-Vis spectroscopy at 329 nm. The absorbance at 329 nm is attributed to 1,5-dihydroxynaphthalene and weakened with the increase of irradiation time. The reaction products were purified by extraction from the reaction mixtures with  $\text{CHCl}_3$ , chromatographing on a silica gel column using  $\text{CHCl}_3$  as eluent and then concentrating the extracts under reduced pressure to give the pure products.

### 2.4. Potentiometric titration of aqueous solution of $\text{H}_2\text{TPPS}^{4-}$

An automatic titrator (Metrohm 751GPD Titrino) coupled to a Metrohm electrode was used and calibrated according to the Gran method [33–35]. The electrode system was calibrated with buffers and checked by titration of  $\text{HClO}_4$  with  $\text{NaOH}$  (0.1 M). All titrations were carried out under an  $\text{N}_2$  atmosphere, at  $25.0 \pm 0.1$  °C and 0.10 M  $\text{NaClO}_4$ . Titrations were performed on the following aqueous solutions with standard  $\text{NaOH}$  solution (0.1 M;  $V_{\text{tot}} = 5$  ml,  $[\text{H}_2\text{TPPS}^{4-}] = 1.0$  mM). Duplicate measurements were performed, for which the experimental error was below 1%. The titration data were fitted with the PSEQUAD program [36] to calculate the formation constants of protonation and deprotonation species for  $\text{H}_2\text{TPPS}^{4-}$ .

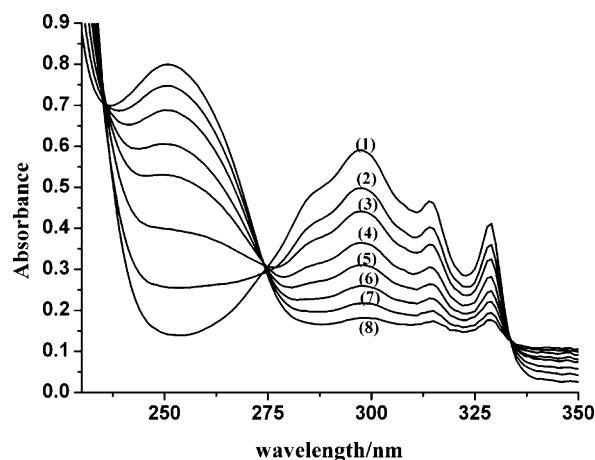


Fig. 1. UV-vis spectra observed during the photodegradation of 1,5-dihydroxynaphthalene catalyzed by  $\text{H}_2\text{TPPS}^{4-}$ . Irradiation time/min: (1) 0; (2) 4; (3) 8; (4) 12; (5) 16; (6) 20; (7) 24; (8) 28.

## 3. Results and discussion

### 3.1. 1,5-dihydroxynaphthalene degradation

Under irradiation of ITL, absorption spectra of 1,5-dihydroxynaphthalene in the presence of  $\text{H}_2\text{TPPS}^{4-}$  at pH 3.8 are given in Fig. 1. It shows that the three absorption bands at 298, 314 and 329 nm attributed to 1,5-dihydroxynaphthalene are weakened, accompanied by a new enhanced absorption band at 251 nm with the increase of irradiation time. It is obvious that 1,5-dihydroxynaphthalene could be decomposed quickly under these conditions. Usually 5-hydroxy-1,4-naphthoquinone is the main photodegraded product of 1,5-dihydroxynaphthalene [22,37,38]. The photodegradation product of 1,5-dihydroxynaphthalene in our system has been characterized and the results are listed in Table 1, which indicates that the product is also 5-hydroxy-1,4-naphthoquinone.

Effect of concentration of 1,5-dihydroxynaphthalene on the absorption at 329 nm was examined (Fig. 2). It can be found that Beer-Lambert law is obeyed for 1,5-dihydroxynaphthalene in the concentrations ranging from 0.02 to 0.18 mM. The Beer-Lambert relationship is shown as an inset in Fig. 2. So we can use the changes of the absorbance of 1,5-dihydroxynaphthalene at 329 nm to calculate photodegradation percentage of 1,5-dihydroxynaphthalene. Fig. 3 shows the effect of  $\text{H}_2\text{TPPS}^{4-}$  concentration on 1,5-dihydroxynaphthalene photodegradation at pH 4.4. In the absence of  $\text{H}_2\text{TPPS}^{4-}$ , 1,5-dihydroxynaphthalene was slightly degraded, while an enhanced photodegradation efficiency of 1,5-dihydroxynaphthalene was observed with the increase of  $\text{H}_2\text{TPPS}^{4-}$ . To evaluate the effect of pH on 1,5-dihydroxynaphthalene photodegradation, a series of experiments were performed at pH ranging from 3.8 to 7.0, and the results are

Table 1  
Characterization data of the photodegradation product of 1,5-dihydroxynaphthalene

Elemental analysis, %	
C	69.11 (68.96) <sup>a</sup>
H	3.55 (3.45) <sup>a</sup>
Mass spectrum, <i>m/z</i>	
	173 ([M-1] <sup>-</sup> )
$^1\text{H}$ NMR ( $\text{CDCl}_3$ , reference to TMS), $\delta$ /ppm	
	6.94(2H, s, H-naph.), 7.26(1H, d, H-naph.), 7.28(1H, d, H-naph.), 7.61(2H, m, H-naph.), 11.87(1H, s, OH)

<sup>a</sup> Calculated from  $\text{C}_{10}\text{H}_6\text{O}_3$ .

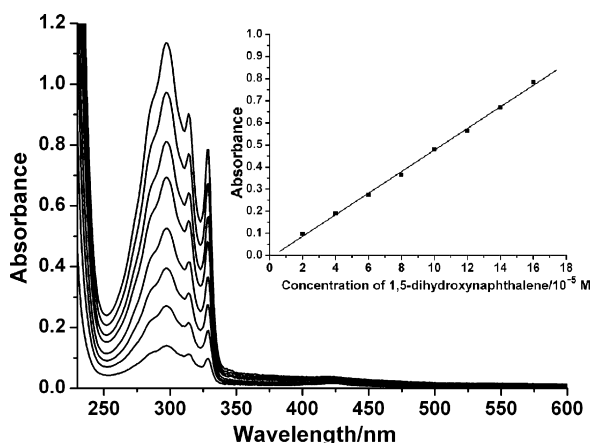


Fig. 2. Changes of the absorbance of 1,5-dihydroxynaphthalene at 329 nm with its concentration and Beer–Lambert law dependence for 1,5-dihydroxynaphthalene.

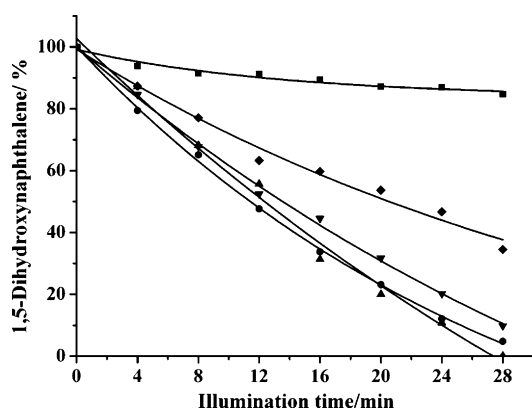


Fig. 3. Effect of initial concentration of  $\text{H}_2\text{TPPS}^{4-}$  on photodegradation of 1,5-dihydroxynaphthalene at pH 4 and 28°C.  $[\text{H}_2\text{TPPS}^{4-}]$ :  $2 \times 10^{-4}$  M (●);  $1 \times 10^{-4}$  M (▲);  $5 \times 10^{-5}$  M (▼);  $2.5 \times 10^{-5}$  M (◆); 0 (■).

shown in Fig. 4. It can be found that 1,5-dihydroxynaphthalene is almost photodegraded completely at pH 3.8 after 20 min irradiation and its photodegradation decreased with the increase of pH. In order to check whether the photodegradation of 1,5-dihydroxynaphthalene at different pH is in fact related to  $\text{H}_2\text{TPPS}^{4-}$ , some blank experiments were conducted, showing no substantial photodegradation of 1,5-dihydroxynaphthalene in absence of  $\text{H}_2\text{TPPS}^{4-}$  at the pH ranging from 3.8 to 7.0. The results further confirm that a dependence of 1,5-dihydroxynaphthalene pho-

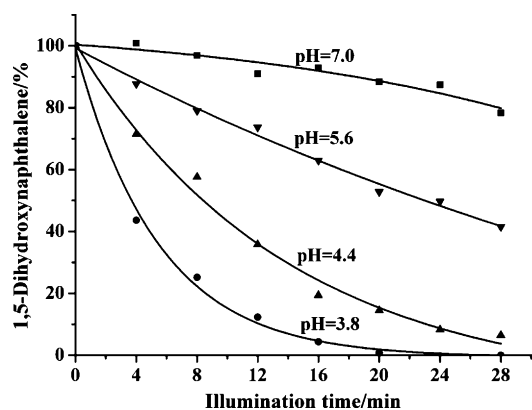


Fig. 4. Effect of pH on photodegradation of 1,5-dihydroxynaphthalene at 28°C.  $[\text{H}_2\text{TPPS}^{4-}]$ :  $1 \times 10^{-4}$  M.

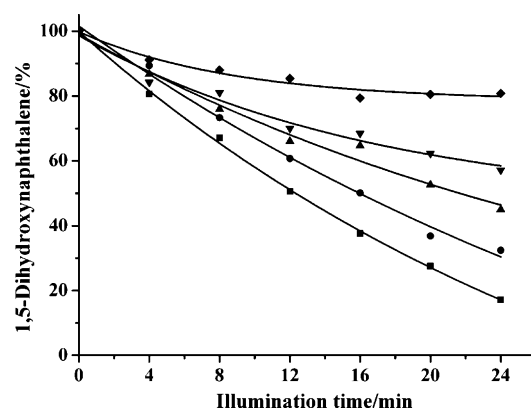


Fig. 5. Effect of  $\text{NaN}_3$  on photodegradation of 1,5-dihydroxynaphthalene at pH 4 and 28°C.  $[\text{H}_2\text{TPPS}^{4-}]$ :  $1 \times 10^{-4}$  M.  $[\text{NaN}_3]$ :  $2.4 \times 10^{-2}$  M (◆);  $1.8 \times 10^{-2}$  M (▼);  $1.2 \times 10^{-2}$  M (▲);  $6 \times 10^{-3}$  M (●); 0 (■).

photodegradation on the pH of aqueous solutions exists in the system we studied here, which may be caused by the change of  $\text{H}_2\text{TPPS}^{4-}$  property at different pH.

It has been suggested that the reactive species responsible for the photooxidation of substrates by oxygen using visible light activation of porphyrin involve singlet oxygen ( $^1\text{O}_2$ ) generated by triplet–triplet energy transfer from excited state of porphyrin to oxygen (type II reaction) or superoxide radical anion ( $\text{O}_2^{\bullet-}$ ) generated by photoinduced electron transfer from excited state of porphyrin to oxygen (type I reaction) [39–42]. In order to identify whether  $^1\text{O}_2$  is involved in the photodegradation of 1,5-dihydroxynaphthalene, we investigated the influence of  $\text{NaN}_3$  on the photodegradation of 1,5-dihydroxynaphthalene. The results show that the degree of 1,5-dihydroxynaphthalene photodegradation decreases significantly in the presence of  $\text{NaN}_3$  and the photodegradation of 1,5-dihydroxynaphthalene decreases with the increase of  $\text{NaN}_3$  (Fig. 5).  $\text{NaN}_3$  is a physical quencher of  $^1\text{O}_2$ . It is obvious that the decrease of the photodegradation of 1,5-dihydroxynaphthalene results from the quenching of singlet oxygen  $^1\text{O}_2$  by  $\text{NaN}_3$ . Thus, the mechanism for the photodegradation of 1,5-dihydroxynaphthalene by  $\text{H}_2\text{TPPS}^{4-}$  is thought to involve singlet oxygen processes, which is similar to the literature about the oxidation of 1,5-dihydroxynaphthalene photosensitized by a set of porphyrins having aromatic groups at the *meso* position in air-saturated acetonitrile–dichloromethane solution [22].

### 3.2. Active species of $\text{H}_2\text{TPPS}^{4-}$ to catalyze photodegradation of 1,5-dihydroxynaphthalene

As described above, a dependence of the photodegradation of 1,5-dihydroxynaphthalene on the pH of aqueous solutions in our system may be related to the change of  $\text{H}_2\text{TPPS}^{4-}$  property at different pH. Protonation and aggregation at specified condition are important properties of  $\text{H}_2\text{TPPS}^{4-}$  [43–45]. Does the dependence of the photodegradation of 1,5-dihydroxynaphthalene on the pH of aqueous solution result from the change of protonation and/or aggregation of  $\text{H}_2\text{TPPS}^{4-}$ ? To confirm the existence of protonation and aggregation of  $\text{H}_2\text{TPPS}^{4-}$  in our system and explore the effect of pH on the protonation and aggregation of  $\text{H}_2\text{TPPS}^{4-}$ , potentiometric titration of  $\text{H}_2\text{TPPS}^{4-}$  was performed. From a fit of the titration data, the formation constants of protonation and deprotonation species for  $\text{H}_2\text{TPPS}^{4-}$  as well as species distribution in solution were obtained. The pH profiles of the titration curves, including the distribution curves of the  $\text{H}_2\text{TPPS}^{4-}$  species as a function of pH are shown in Fig. 6. Five species can be found in the pH ranging from 2.5 to 11.5 in

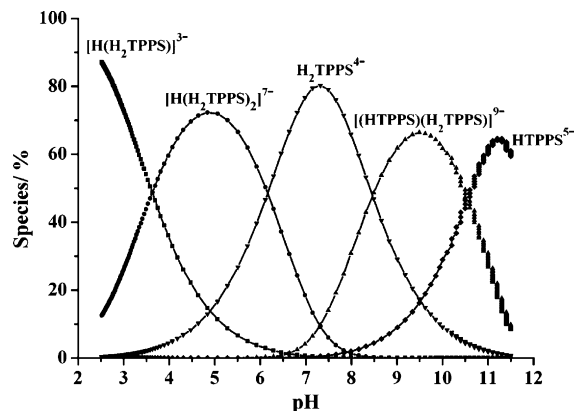


Fig. 6. Distribution plots for the species of  $H_2TPPS^{4-}$  as a function of pH in the presence of 0.1 M  $NaClO_4$  at  $25 \pm 0.1^\circ C$ .

Fig. 6. These species include mono-protonated monomeric species  $[H(H_2TPPS)]^{3-}$ , mono-protonated dimeric species  $[H(H_2TPPS)_2]^{7-}$ , natural species  $H_2TPPS^{4-}$ , mono-deprotonated dimeric species  $[(HTPPS)(H_2TPPS)]^{9-}$  and mono-deprotonated monomeric species  $HTPPS^{5-}$ . Fig. 6 also indicates the dependence of the species on the pH of the solution. The natural species  $H_2TPPS^{4-}$  is the predominant species over the pH range of 6.1–8.4 (maximum at pH 7.3). The natural species  $H_2TPPS^{4-}$  can protonate at lower pH. The mono-protonated monomeric species  $[H(H_2TPPS)]^{3-}$  and the mono-protonated dimeric species  $[H(H_2TPPS)_2]^{7-}$  are the major complexes in solution at  $2.5 < pH < 6.1$  (maximum at pH 2.4 and 4.8, respectively). On the contrary, the natural species  $H_2TPPS^{4-}$  can also be deprotonated at higher pH. The mono-deprotonated dimeric species  $[(HTPPS)(H_2TPPS)]^{9-}$  and the mono-deprotonated monomeric species  $HTPPS^{5-}$  become the major species in solution at  $pH > 8.4$  (maximum at pH 9.5 and 11.2, respectively). The protonation and deprotonation of  $H_2TPPS^{4-}$  involve in the nitrogen atoms in the core of porphyrin ring [43]. The dimeric species  $[H(H_2TPPS)_2]^{7-}$  and  $[(HTPPS)(H_2TPPS)]^{9-}$  may be the J-aggregated species which form through an interaction between the positive charged core of a porphyrin unit and the negative sulfonate groups of neighboring one [45]. We propose that five species of  $H_2TPPS^{4-}$  in aqueous solution are in equilibrium as following:

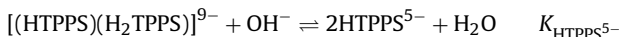
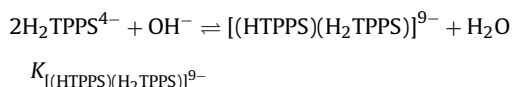
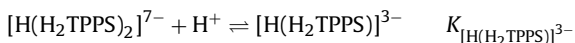
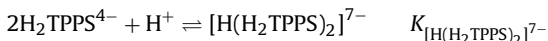


Table 2

Formation constants of protonation or deprotonation species for  $H_2TPPS^{4-}$  at  $I = 0.1$  M  $NaClO_4$  and  $25 \pm 0.1^\circ C$

Formation constants, $K$	$\log K$
$K_{[H(H_2TPPS)_2]^{7-}}$	$10.68 \pm 0.04$
$K_{[H(H_2TPPS)]^{3-}}$	$0.60 \pm 0.08$
$K_{[(HTPPS)(H_2TPPS)]^{9-}}$	$9.99 \pm 0.07$
$K_{HTPPS^{5-}}$	$0.29 \pm 0.04$

$\log K_w$  is  $-13.92$  obtained by potentiometric pH titration at  $I = 0.1$  M  $NaClO_4$  and  $25 \pm 0.1^\circ C$ .

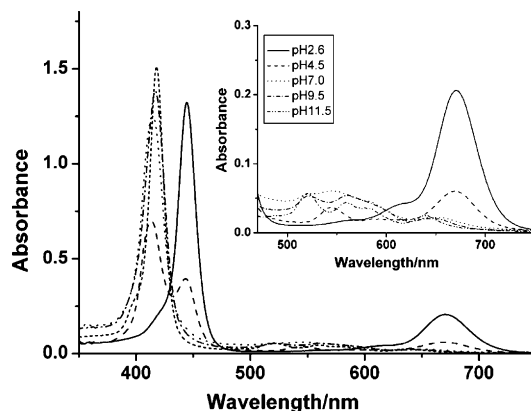


Fig. 7. Normalized absorption spectra for  $H_2TPPS^{4-}$  in different pH.

The formation constants of these species obtained from potentiometric titration are summarized in Table 2.

UV-vis spectra of the major species at corresponding pH provide another evidence for the presence of the five species of  $H_2TPPS^{4-}$  in aqueous solution. As shown in Fig. 7, there are obvious differences among the UV-vis spectra of  $H_2TPPS^{4-}$  at different pH under our experimental conditions. For example, it can be found that  $[H(H_2TPPS)]^{3-}$  species absorbs mainly at 444/671 nm,  $[H(H_2TPPS)_2]^{7-}$  species absorbs mainly at 413/443/669 nm,  $H_2TPPS^{4-}$  species absorbs mainly at 415/546 nm,  $[(HTPPS)(H_2TPPS)]^{9-}$  species absorbs mainly at 417/521 nm and  $HTPPS^{5-}$  absorbs mainly at 415/520/559 nm.

Fig. 4 has indicated that the photodegradation of 1,5-dihydroxynaphthalene decreases with the increase of pH and  $H_2TPPS^{4-}$  has the highest catalytic activity especially at pH 3.8. Are there a relationship between the catalytic activity and the kinds of species of  $H_2TPPS^{4-}$  at different pH? Considering the photodegradation of 1,5-dihydroxynaphthalene and the species distribution at different pH, a trend that the photodegradation of 1,5-dihydroxynaphthalene varies with the percentages of  $[H(H_2TPPS)]^{3-}$  species can be observed. The percentages of  $[H(H_2TPPS)]^{3-}$  species at pH 3.8, 4.4, 5.6 and 7.0 can be obtained from Fig. 6, which are 42.13, 23.35, 5.56 and 0.50, respectively. We make a plot of the percentages of degraded 1,5-dihydroxynaphthalene after 4 min irradiation calculated from Fig. 4 against the percentages of  $[H(H_2TPPS)]^{3-}$  species at corresponding

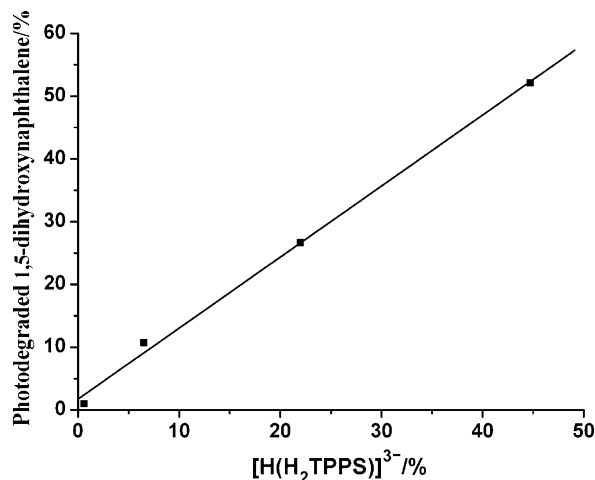


Fig. 8. Plot of the percentages of degraded 1,5-dihydroxynaphthalene after 4 min irradiation against the percentages of  $[H(H_2TPPS)]^{3-}$  species at corresponding pH.



pH (Fig. 8). To our surprise, Fig. 8 shows a linear dependence of the percentages of photodegraded 1,5-dihydroxynaphthalene on the percentages of  $[H(H_2TPPS)]^{3-}$  species. So we can conclude that the mono-protonated monomeric species  $[H(H_2TPPS)]^{3-}$  is the main active species of  $H_2TPPS^{4-}$  to catalyze photodegradation of 1,5-dihydroxynaphthalene.

#### 4. Conclusions

The photodegradation of 1,5-dihydroxynaphthalene catalyzed by meso-tetra(4-sulfonatophenyl)porphyrin  $H_2TPPS^{4-}$  under visible light irradiation in aerated aqueous solution has been studied and is shown to lead to formation of 5-hydroxy-1,4-naphthoquinone as main photoproduct. The photodegradation is dependent on the pH of reaction system. The experiments carried out in the presence of  $NaN_3$  as a singlet oxygen quencher showed a significant decrease in the degree of photodegradation of 1,5-dihydroxynaphthalene, suggesting that under these conditions, Type II sensitization may be one of the dominant mechanisms for photodegradation of 1,5-dihydroxynaphthalene. Considering the dependence of the photodegradation to the pH of reaction system and the species distribution of  $H_2TPPS^{4-}$  in solution obtained from potentiometric titration experiments, it is suggested that the mono-protonated monomeric species  $[H(H_2TPPS)]^{3-}$  is the main active species of  $H_2TPPS^{4-}$  to catalyze photodegradation of 1,5-dihydroxynaphthalene.

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