

## A Comparative Kinetic Study of the Photo-oxidation of Phenol by Tetra-cationic Porphyrins and Zinc Compounds

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### ABSTRACT

Kinetic of the photo-oxidation of phenol in aqueous alkaline and neutral buffer solutions was studied and compared by irradiation of visible light in the presence of tetra-cationic porphyrins and their zinc metal ion photo-sensitizers. The porphyrins 5,10,15,20-tetrakis(3-methylpyridinium)porphyrin (TMPyP<sub>(3)</sub>); 5,10,15,20-tetrakis(4-methylpyridinium)porphyrin (TMPyP<sub>(4)</sub>); 5,10,15,20-tetrakis(4-*N,N,N*-trimethylanilinium)porphyrin (TAPP) and their zinc ion complexes were used in this study. In the dark conditions, none of the porphyrin compounds showed any effect on the reducing of phenol. The results showed that the rate of the photo-oxidation of phenol in alkaline medium has been increased in the presence of these photo-sensitizers. Among them, the rate of photo-oxidation by TAPP was more than the other ones. In neutral medium, the rate of the photo-oxidation of all of the compounds have been shown approximately similar behavior. It was found that the dominant pathway of phenol degradation occurred in the reaction with molecular singlet oxygen (<sup>1</sup>O<sub>2</sub>). Kinetic parameters of the phenol reaction with <sup>1</sup>O<sub>2</sub> were estimated. According to the equation ( $\ln A/A_0 = k_{\text{obs}} t$ ) and by plotting  $\ln A/A_0$  against time, the rate of the reaction was obtained first order.

**Keywords:** Kinetic study, Photo-oxidation of phenol, Photo-sensitizer, Tetra-cationic porphyrin, Zinc porphyrin

### INTRODUCTION

Phenol and its derivatives are one of the most important main pollutants and toxic substances in industrial wastewater. Even, low concentrations of these compounds could be harmful to organisms [1,2].

The oxidation of phenol derivatives is one of the most interesting fields of research to scientists and is known to be important chemicals in the pharmaceutical and dye industries [3]. Phenol compounds could be reacted with singlet oxygen [4,5]. The main oxidation product is hydroperoxides that is dehydrate to form benzoquinone and *p*-hydroquinone [6]. On the other hand, the kinetic study and the effect of various compounds have been studied for degradation of them [1,7-10].

The effect of various macrocyclic systems such as

porphyrins or metalloporphyrins has been reported to be a powerful process in the photo-oxidation of phenol derivatives [4,5,11,12]. Neutral porphyrins and chlorine, hybrid photo-sensitizer with porphyrin, metalloporphyrins with Fe, Zn and Cu have been used for this purpose [6,11,13,14].

Also, porphyrin compounds have great potential as photo-therapeutic agents for the treatment of a variety of diseases due to absorption of photons in the visible region and the production of singlet oxygen (<sup>1</sup>O<sub>2</sub>) [15-17]. <sup>1</sup>O<sub>2</sub> is a highly electrophilic compound and capable of oxidizing phenols, sulfides, and amines [4,8,9]. The mechanism of reactive oxygen species (ROS) formation by porphyrins involves electronic excitations of the molecule to the first singlet excited state, followed by intersystem crossing with the formation of excited triplet state which is quenched by molecular oxygen. At the end of this sequence, the porphyrin molecule returns to the ground state and singlet

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oxygen is formed [18-22].

Our aim was to investigate the aqueous degradation of phenol in the photo-oxidation process using tetracationic porphyrins and their zinc compounds as photo-sensitizers. The obtained results were used to estimate kinetic parameters of photo-sensitized oxidation.

## EXPERIMENTAL

### Materials and Methods

All of the used chemicals except porphyrins were purchased from Merck and used without further purification. 5,10,15,20-tetrakis(4-*N,N*,dimethylanilinium) porphyrin; 5,10,15,20-tetrakis(3-pyridyl) porphyrin (TPyP<sub>(3)</sub>) and 5,10,15,20-tetrakis(4-pyridyl)porphyrin (TPyP<sub>(4)</sub>) were purchased from MidCentury (Chicago, Illinois). For buffers with pH = 7.2 and pH = 9.2, phosphate and borate buffers were used respectively, and the pH of the solutions was adjusted by a model 827 pH Lab Metrohm Swiss made. UV-Vis absorption spectra were measured on a T80 + UV-Vis Spectrometer PG instruments Ltd. with a quartz cuvette. <sup>1</sup>H NMR spectra were obtained at 300 MHz (Bruker) instrument. The FT-IR measurements were carried out with the help of Shimadzu FT-IR spectrometer in the form of KBr pellets. All the experiments were carried out in a water-jacked reactor irradiated with a 100 W tungsten lamp as a visible light source at a distance of 20 cm from the sample. To avoid light reflection, the reactor was placed in a dark room. The laboratory temperature was 25 ± 2 °C with relative humidity (RH) of 60 ± 2%. The information of <sup>1</sup>H NMR, FT-IR and UV-Vis spectra of the used porphyrin compounds were recorded and given as follow:

**TMPyP<sub>(3)</sub>.** <sup>1</sup>H NMR (D<sub>2</sub>O) δ: 4.53 (s, 12H); 8.44 (t, 4H); 8.92 (s, 8H); 9.23 (d, 4H); 9.30 (d, 4H); 9.71 (s, 4H); FT-IR (cm<sup>-1</sup>): 700-900 (porphyrin ring vibration), 975 (N-H bending), 1000-1300 (C-N stretching), 1475-1600 (C=C stretching), 1631 (C=N stretching), 2920 (C-H stretching), 2952 (N-H stretching); UV-Vis in H<sub>2</sub>O (λ<sub>max</sub>, nm): 417, 516, 550, 582, 642 nm.

**TMPyP<sub>(4)</sub>.** <sup>1</sup>H NMR (D<sub>2</sub>O) δ: 4.65 (s, 12H); 8.80 (d, 8H); 9.05 (d, 8H); 9.17 (d, 8H); FT-IR (cm<sup>-1</sup>): 700-900 (porphyrin ring vibration), 970 (N-H bending), 1000-1300 (C-N stretching), 1400-1500 (C=C stretching), 1637 (C=N stretching), 2952 (C-H stretching), 3031 (N-H stretching);

UV-Vis in H<sub>2</sub>O (λ<sub>max</sub>, nm): 422, 515, 554, 556, 641 nm.

**TAPP.** <sup>1</sup>H NMR (D<sub>2</sub>O) δ: 3.66 (s, 36H); 8.09 (d, 16H); 8.68 (s, 8H); FT-IR (cm<sup>-1</sup>): 700-900 (porphyrin ring vibration), 900 (N-H bending), 1000-1300 (C-N stretching), 1469, 1487 (C=C stretching), 1606 (C=N stretching), 3029 (N-H stretching); UV-Vis in H<sub>2</sub>O (λ<sub>max</sub>, nm): 412, 515, 552, 580, 634 nm.

**ZnTMPyP<sub>(3)</sub>.** <sup>1</sup>H NMR (D<sub>2</sub>O) δ: 4.60 (s, 12H); 8.36 (t, 4H); 8.91 (s, 8H); 9.16 (d, 4H); 9.24(d, 4H); 9.64(s, 4H); FT-IR (cm<sup>-1</sup>): 700-900 (porphyrin ring vibration), 1000 (Zn-N stretching), 1000-1300 (C-N stretching), 1475-1600 (C=C stretching), 1633 (C=N stretching), 2966 (C-H stretching); UV-Vis in H<sub>2</sub>O (λ<sub>max</sub>, nm): 428, 558, 594.

**ZnTMPyP<sub>(4)</sub>.** <sup>1</sup>H NMR (D<sub>2</sub>O)δ: 4.35 (s, 12H); 8.50 (d, 8H); 8.75 (d, 8H); 8.87 (d, 8H); FT-IR (cm<sup>-1</sup>): 700-900 (porphyrin ring vibration), 1000 (Zn-N stretching), 1000-1300 (C-N stretching), 1400-1500 (C=C stretching), 1639 (C=N stretching), 2923 (C-H stretching); UV-Vis in H<sub>2</sub>O (λ<sub>max</sub>, nm): 436, 563, 606.

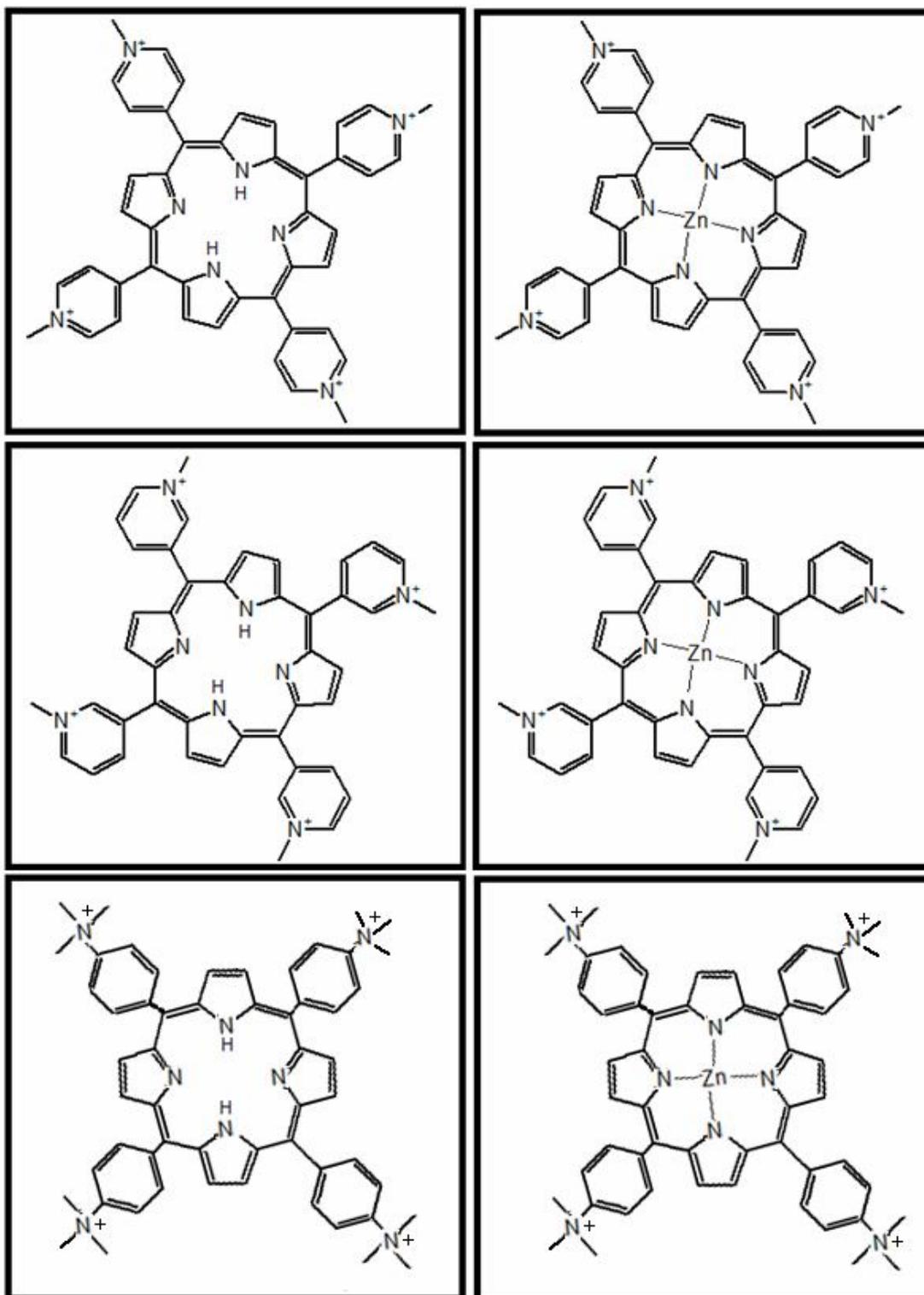
**ZnTAPP.** <sup>1</sup>H NMR (D<sub>2</sub>O) δ: 3.36 (s, 36H); 7.68 (s, 8H); 7.38 (s, 8H); 8.53 (s, 8H); FT-IR (cm<sup>-1</sup>): 700-900 (porphyrin ring vibration), 1000-1300 (C-N stretching), 1473, 1494 (C=C stretching), 1606 (C=N stretching); UV-Vis in H<sub>2</sub>O (λ<sub>max</sub>, nm): 421, 556, 596.

### Photo-stability Study of Prepared Porphyrins

The photo-stability of prepared porphyrins at concentration 5 × 10<sup>-6</sup> M was determined in buffer media with the appropriate pH (7.2 or 9.2) upon illumination with the light source according to our previous work [23]. During irradiation, the solution was magnetically stirred at room temperature. The concentration of the porphyrin samples was monitored spectrophotometrically at times 0, 15, 30, 60 and 90 min and the photo-stability was expressed as the percentage residual absorbance compared to absorbance measured before irradiation.

### Photo-oxidation of Phenol by Photo-sensitizers

An aqueous solution of phenol at a concentration of 1 × 10<sup>-3</sup> M was mixed with equal amounts of porphyrin solution at a concentration of 1 × 10<sup>-5</sup> M in buffer media with the appropriate pH (7.2 or 9.2). The solutions were illuminated for 90 min with the light source. Also, the oxidation of phenol by these compounds was evaluated in



**Fig. 1.** Chemical structure of used porphyrin compounds.

the dark conditions as control samples.

At various minute intervals, sample solutions (~ 2 ml) were removed and the absorption spectrum was measured in the range of 190-340 nm. In this area, the phenol solutions are shown maximum wavelength.

### Kinetic Study of Photo-oxidation of Phenol

Kinetic study of the photo-oxidation of phenol, were done as described in the above section. We used the equation ( $\ln A/A_0 = k_{\text{obs}} t$ ) for determination empirical constant rate ( $k_{\text{obs}}$ ) for photo-oxidation of phenol, in which  $A$  is the amount of the absorbance of the product photo-oxidation of phenol (*p*-benzoquinone) at exposure time,  $A_0$  shows the absorbance of solution at first time. By plotting  $\ln A/A_0$  against time and determination  $k_{\text{obs}}$ , the potential of photo-oxidation of phenol by these tetra-cationic porphyrins (production singlet oxygen) could be determined and compared.

## RESULTS AND DISCUSSION

The chemical structure of three tetra-cationic porphyrins and metalloporphyrin derivatives is shown in Fig. 1. The photo-stability study of these porphyrins at concentration  $5 \times 10^{-6}$  M was determined in the buffer medium at (pHs = 7.2 and 9.2) upon illumination after 15, 30, 60 and 90 min with the irradiation system; the results is shown in Fig. 2. Photo-stability is expressed as the percentage residual absorbance relative to the absorbance measured before irradiation. At pH = 7.2 and after 90 min irradiation, the percent residual photo-stability of photo-sensitizers were determined to be 60.6, 70.6, 76.6, 80.6, 89.2 and 95% for ZnTAPP, ZnTMPyP(4), TMPyP(4), ZnTMPyP(3), TMPyP(3) and TAPP, whereas at pH = 9.2 under the same conditions, were 48.7, 55.2, 63.6, 59.6, 49.3 and 71% respectively. It seems that, the photo-stability of these photo-sensitizers is reduced in alkaline medium and TAPP has more photo-stability than the others in both mediums.

To study the photo-oxidation of phenol, aqueous solutions were prepared at two pHs (7.2 and 9.2) and illuminated by the light source as described. At various minute intervals samples (~ 2 ml) were removed and the absorption spectra were measured in the range of 190-340 nm. No remarkable changes were observed in UV-Vis

spectrum of the phenol solution with the studied light source in this work. The light is absorbed only by the porphyrin chromospheres present in the system. The irradiation of the system at pH = 7.20 resulted in the appearance of a new absorption band at  $\lambda = 238$  nm for all porphyrin compounds. The rate of the process increased at pH = 9.20 and the new band was observed at  $\lambda = 245$  nm. The new absorption band at pH = 9.20 for TAPP formed completely; but in the case of the other photo-sensitizers, it was not completed (Fig. 3).

The new absorption band at  $\lambda = 245$  nm (pH = 9.20) and  $\lambda = 238$  nm (pH = 7.20) corresponded to *p*-benzoquinone [4,5,8,11]. To prove this claim, we were recording the UV-Vis spectrum of pure *p*-benzoquinone in water and the maximum wavelength of this compound was 245 nm.

We were observed that alkaline pH is an effective factor for the photo-oxidation of phenol according to an article [11]. Alkaline pH improves the speed of the formation *p*-benzoquinone and also the degree of phenol dissociation to phenoxide can be increased in this condition. Also, our observations were shown that in alkaline pH, the photo-sensitizers could be more effective than at neutral pH. The absorption bands of phenol in alkaline pH are shown two shoulders, which corresponded to the degree of dissociation of phenol and formation of phenoxide.

In the dark conditions, none of the porphyrin compounds showed any effect on reducing the phenol. The production of singlet oxygen by these compounds plays an important role in the mechanism of action of porphyrins under the light conditions. Clearly, the exact mechanism of action of porphyrin compounds needs further investigation. It seems that various factors could affect this mechanism, such as binding of the photo-sensitizer, illumination time and *etc.*

For kinetic study, the rate of photo-oxidation of phenol by singlet oxygen produced by these porphyrin compounds calculated by plotting  $\ln A/A_0$  against time at  $\lambda = 245$  nm (pH = 9.20) and  $\lambda = 238$  nm (pH = 7.20) corresponded to *p*-benzoquinone. The slope of the plot shows the empirical constant rate of reaction ( $k_{\text{obs}}$ ) for production *p*-benzoquinone (Fig. 4).

In these figures, the slope of the points was determined using the Excel software. The results were shown that the photo-oxidation rate of phenol by these porphyrins increased by exposure time. Also, the values of  $k_{\text{obs}}$  state

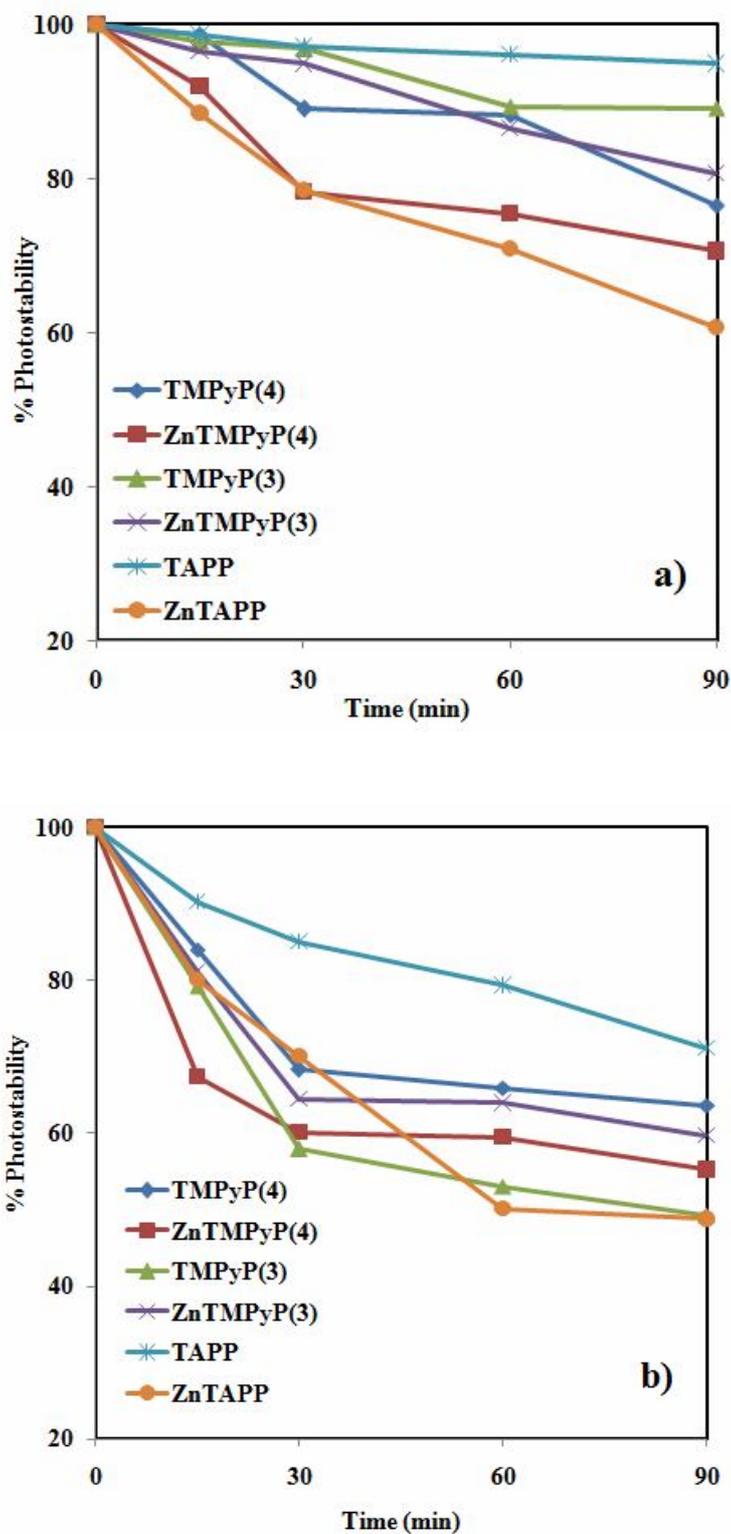


Fig. 2. The percent of photo-stability of used porphyrin compounds at pH = 9.2 (a) and at pH = 7.2 (b).

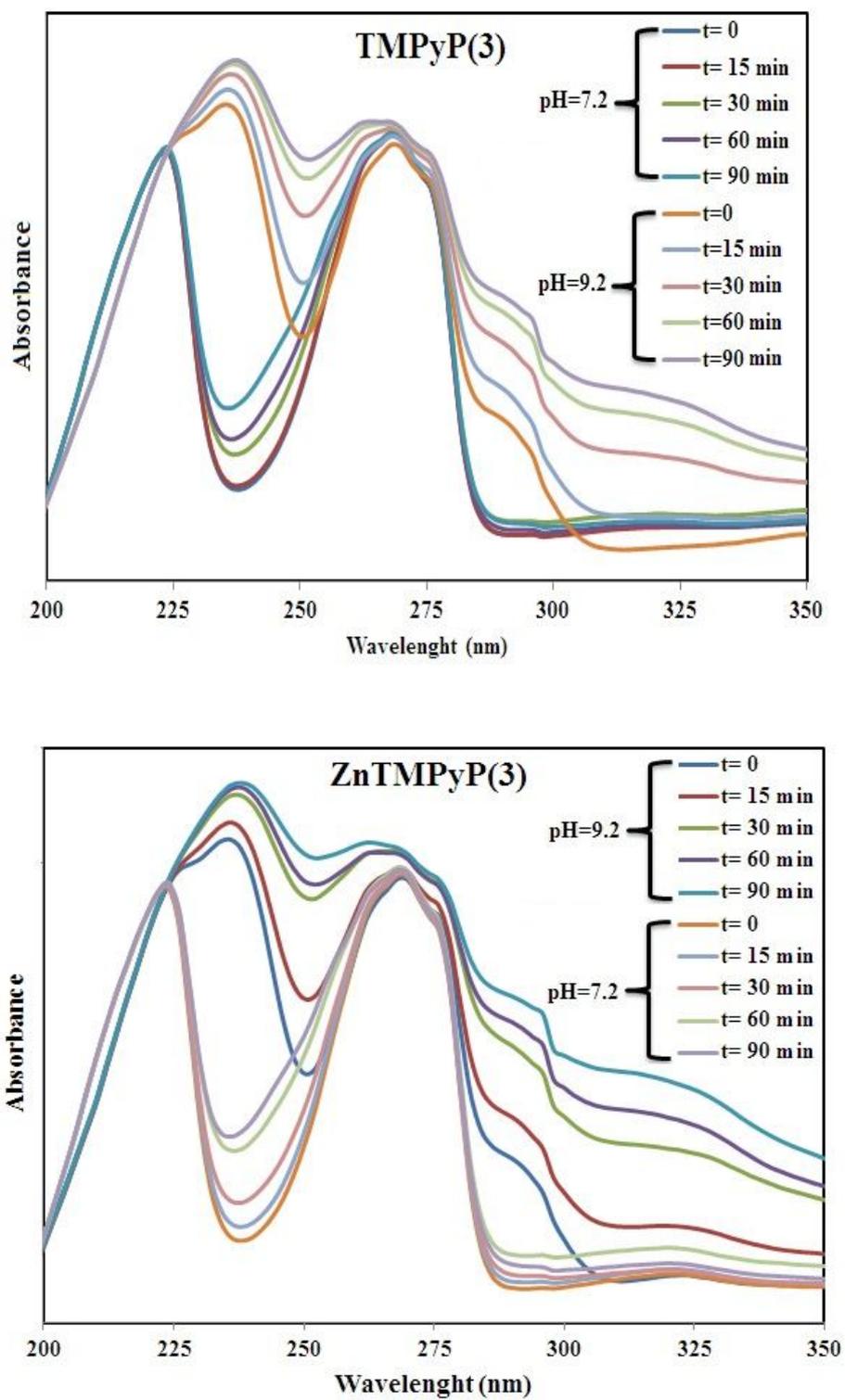


Fig. 3. The effect of porphyrin compounds on photo-oxidation of phenol at pH = 7.2 and pH = 9.2.

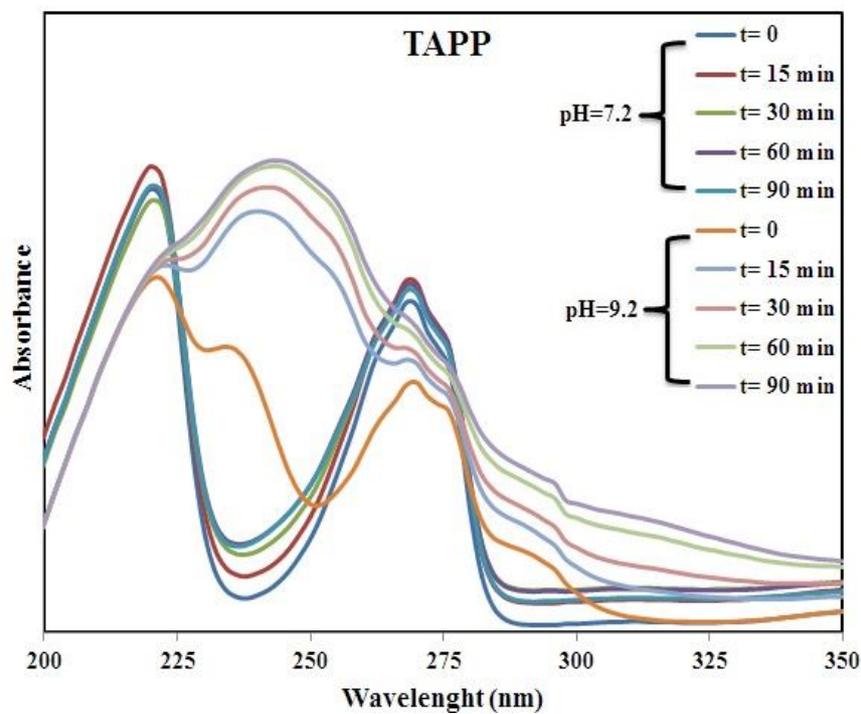
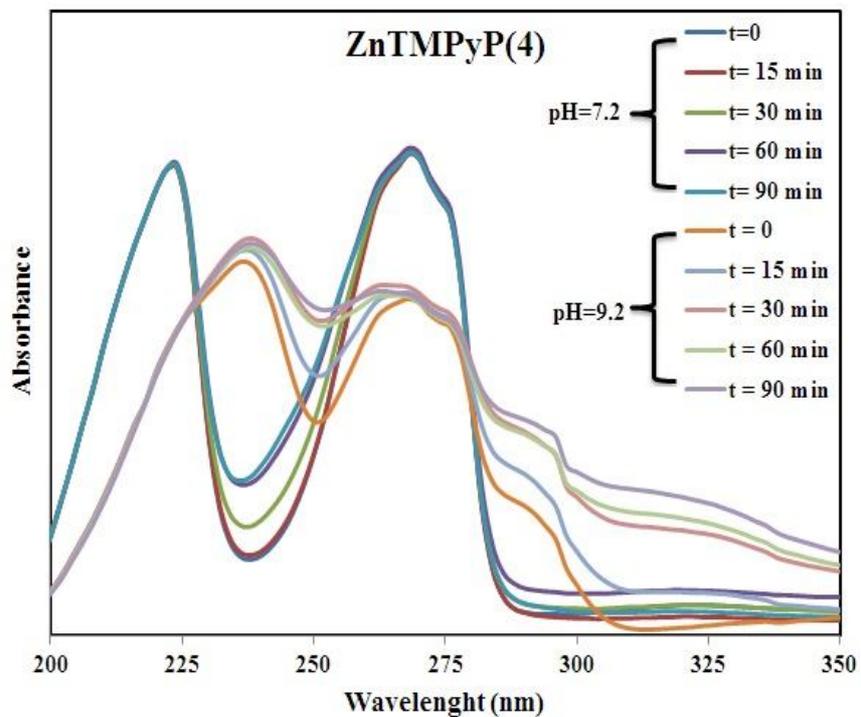


Fig. 3. Continued.

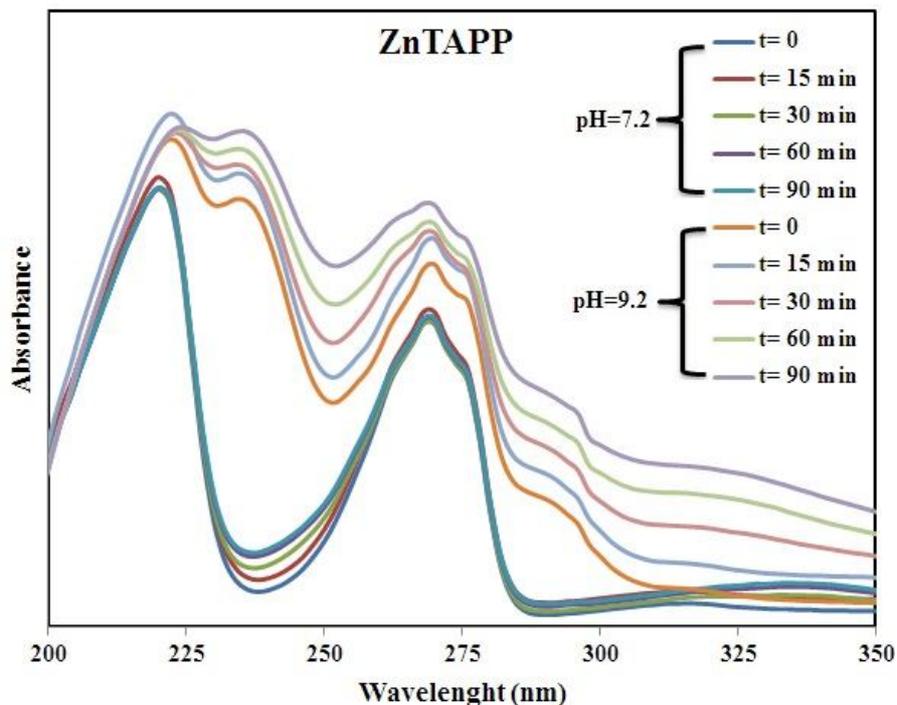


Fig. 3. Continued.

**Table 1.** The Effect of Various Tetra-cationic Porphyrins on Values of  $k_{obs}$  ( $\text{min}^{-1}$ )

Entry	Photosensitizes	$K_{obs}$ (pH = 7.2)	$K_{obs}$ (pH = 9.2)
1	TMPyP <sub>(3)</sub>	0.0072( $\pm$ 0.002)	0.0137( $\pm$ 0.004)
2	TMPyP <sub>(4)</sub>	0.0084( $\pm$ 0.0025)	0.0116( $\pm$ 0.002)
3	TAPP	0.0092( $\pm$ 0.0011)	0.0732( $\pm$ 0.003)
4	ZnTMPyP <sub>(3)</sub>	0.009( $\pm$ 0.0016)	0.0172( $\pm$ 0.004)
5	ZnTMPyP <sub>(4)</sub>	0.0091( $\pm$ 0.0015)	0.0128( $\pm$ 0.002)
6	ZnTAPP	0.0055( $\pm$ 0.0004)	0.0093( $\pm$ 0.0005)

that alkaline medium could be effective as an influential factor for photo-oxidation and production of singlet oxygen. The period time of photo-oxidation by TAPP is faster than the other compounds. TAPP could be converted completely phenol to *p*-benzoquinone at a short time of irradiation. Probably, this compound has a better ability to produce

singlet oxygen in an alkaline environment.

Table 1 shows the effect of various tetra-cationic porphyrins on values of  $k_{obs}$ . In neutral pH, the photo-oxidation rate of the all compounds ( $k_{obs}$ ) is similar. This shows that the photo-oxidation ability of all studied tetra-cationic porphyrin compounds approximately is equal

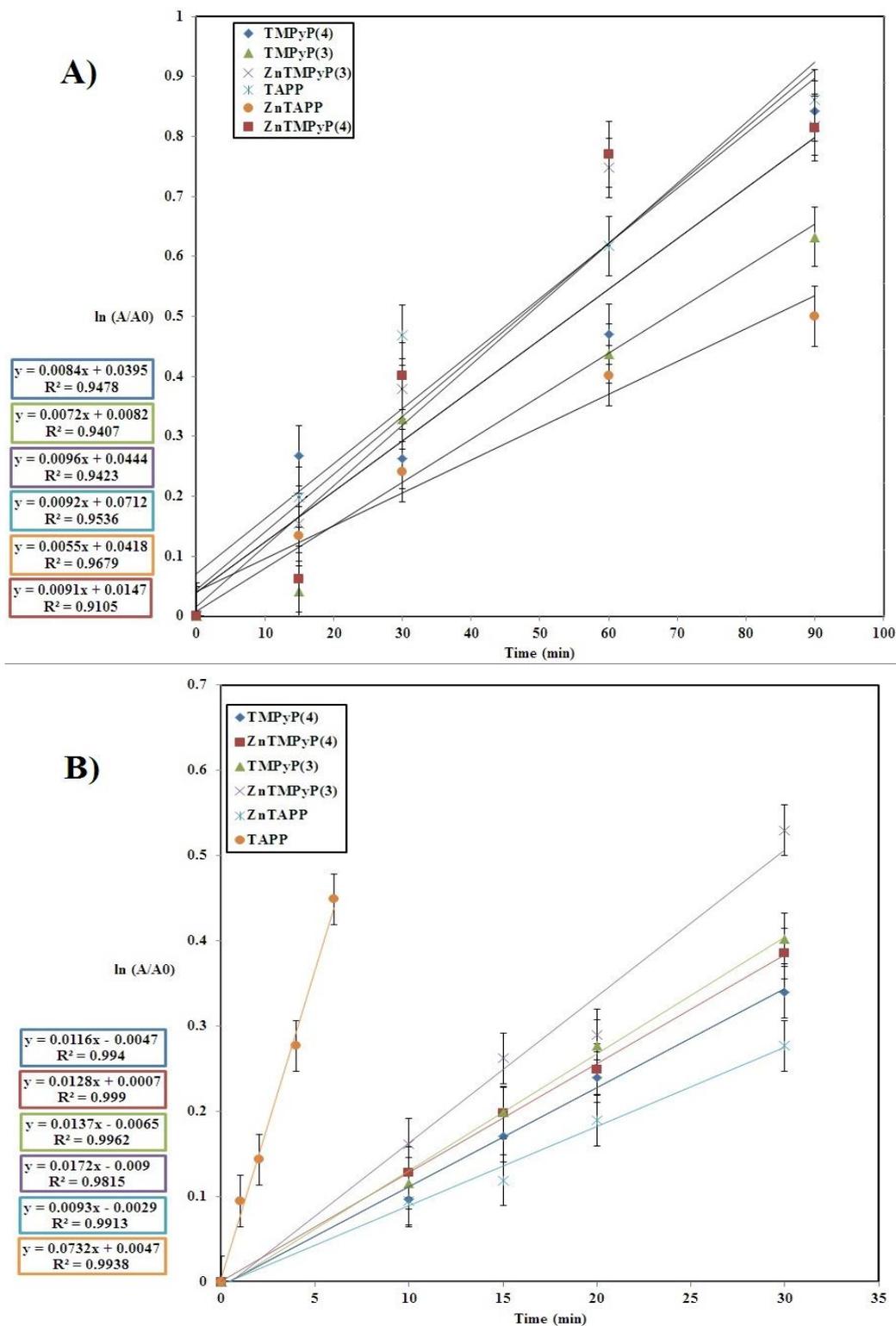


Fig. 4. The kinetic study of the photo-oxidation of phenol by tetra-cationic porphyrins at A) pH = 7.2 and B) pH = 9.2.

(Fig. 4). In alkaline pH, the photo-oxidation rate of photosensitizers would be different. In this medium, the production rate of singlet oxygen or the photo-oxidation of phenol is followed: TAPP > ZnTMPyP<sub>(3)</sub> > TMPyP<sub>(3)</sub> > ZnTMPyP<sub>(4)</sub> > TMPyP<sub>(4)</sub> > ZnTAPP.

Our experimental results show that TAPP is the best compound for perfect photo-oxidation of phenol to the other compounds. This research has several advantages, such as low power using, inexpensive irradiation system; and a lower reducing the response dose and irradiation time for photo-oxidation of phenol.

There are two types of mechanisms for oxidation of pollutants by photo-sensitizers. Type I involves direct interaction between the triplets excited sensitizer and organic compounds. Radical ions are formed as a result of electron or hydrogen transfer and they can undergo reaction with oxygen. The type II mechanism involves energy transfer from the triplet excited photosensitizer to the triplet molecular oxygen, generating singlet oxygen, which can oxidize water pollutants such as phenol compounds. Porphyrins or metalloporphyrins such as metal phthalocyanines, tetraphenylporphyrine, rose Bengal or methylene blue have been reported to be powerful compounds used in the photo degradation-oxidation of various phenol compounds. They are shown to lead to formation of *p*-benzoquinone and *p*-hydroquinone as main photoproducts [12,24,25].

According to the experimental results in dark conditions, none of the studied porphyrin compounds showed any effect on reducing the phenol; it seems that the production of singlet oxygen by these tetra-cationic porphyrins plays an important role in the photo-oxidation of phenol under the light conditions.

As a result, the mechanism of singlet oxygen formation by these studied porphyrins involves electronic excitations of their molecules to the first singlet excited state, followed by intersystem crossing with the formation of excited triplet state which is quenched by molecular oxygen. At the end of this sequence, the porphyrin molecule returns to the ground state and singlet oxygen is formed [12,19-23,25,26]. The production of singlet oxygen plays an important role in the mechanism of action of porphyrins under light conditions. This molecule is able to react with phenol compounds, leading to formation of

*p*-benzoquinone and *p*-hydroquinone as main photoproducts [26].

## CONCLUSIONS

In summary, the kinetic study of the photo-oxidation of phenol by irradiation with visible light in aqueous alkaline and neutral solutions in the presence of tetra-cationic porphyrin photo-sensitizers was investigated spectrophotometrically. The photo-sensitizers exhibited different activities in alkaline medium and similar in neutral medium. None of the porphyrin compounds were affected on photo-oxidation of phenol in dark condition. It was found that TAPP was a suitable singlet oxygen generator. A new absorption band at  $\lambda = 245$  nm (pH = 9.20), confirmed the production of *p*-benzoquinone as a photochemical product.

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