

Photocatalysis of 4-nitrophenol using zinc phthalocyanine complexes

Eloïse Marais, Rosalyn Klein, Edith Antunes, Tebello Nyokong*

Department of Chemistry, Rhodes University, P.O. Box 94, Grahamstown 6140, South Africa

Received 5 June 2006; received in revised form 18 July 2006; accepted 19 July 2006

Available online 1 September 2006

Abstract

Photodegradation of 4-nitrophenol (4-Np) in the presence of zinc tetrasulfophthalocyanine (ZnPcS_4), zinc octacarboxyphthalocyanine ($\text{ZnPc}(\text{COOH})_8$) and a sulfonated ZnPc containing a mixture of differently sulfonated derivatives ($\text{ZnPcS}_{\text{mix}}$), as photocatalysts is reported. $\text{ZnPcS}_{\text{mix}}$ is the most effective catalyst in terms of a high quantum yield for 4-Np degradation and the stability of the catalyst. However $\text{ZnPc}(\text{COOH})_8$ degrades readily during the catalysis, but it has a higher quantum yield ($\Phi_{4\text{-Np}}$) for 4-Np degradation than the rest of the complexes. The $\Phi_{4\text{-Np}}$ values were closely related to the singlet oxygen quantum yields Φ_{Δ} and hence aggregation. The rate constants for the reaction with 4-Np were $k_r = 0.67 \times 10^6 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ for $\text{ZnPcS}_{\text{mix}}$ and $2.8 \times 10^8 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ for $\text{ZnPc}(\text{COOH})_8$.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Nitrophenol; Phthalocyanine; Photocatalysis; Aggregation; Quantum yields

1. Introduction

Nitrophenols are of interest due to their inclusion as priority toxic pollutants by agencies such as the United States Environmental Protection Agency. Nitrophenols are employed for the synthesis of many products and are also the degradation products of pesticides such as parathion and nitrofen. The interest in nitrophenols is due to their high stability and solubility in water as well as their resistance to traditional methods of water purification. Microbial degradation of nitrophenols is a time-consuming process [1]. 4-Nitrophenol (4-Np) was selected for study in this work since it is produced in high quantities worldwide [2].

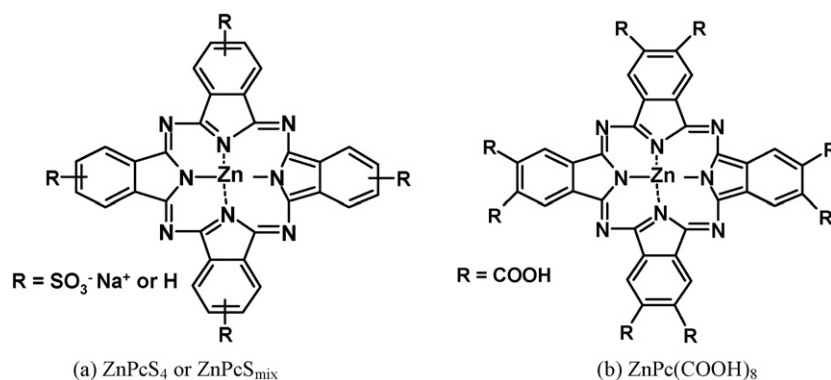
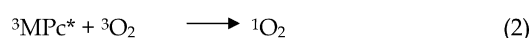
Metallophthalocyanines (MPcs) containing non-transition metals are efficient photocatalysts for many pollutants including phenols. The most accepted reaction mechanism for the photodegradation of phenolic compounds involves the interaction of the excited triplet MPc sensitizer ($^3\text{MPc}^*$) with ground state oxygen to produce active singlet oxygen ($^1\text{O}_2$), through the so-called type II mechanism. This occurs via the triplet–triplet energy transfer process, Eqs. (1)–(3), Scheme 1 [3].

The other possible route involves the participation of a superoxide radical through the so-called type I mechanism, Eqs. (4)–(9), Scheme 2 [4,5].

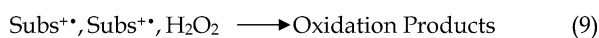
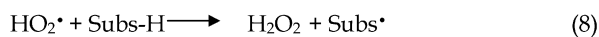
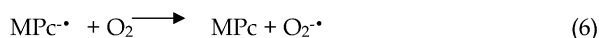
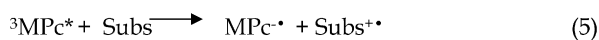
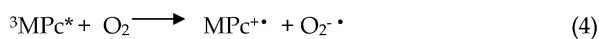
Non-transition MPcs are effective for photocatalysis since they produce singlet oxygen (essential for type II mechanism) in high quantum yields. Water-soluble MPcs are required for photodegradation to occur in aqueous media, and they may be formed by substitution of the Pc ring with negatively or positively charged substituents. In this work, three water soluble ZnPc complexes are employed. These are the zinc tetrasulfophthalocyanine (ZnPcS_4), zinc octacarboxyphthalocyanine ($\text{ZnPc}(\text{COOH})_8$) and a sulfonated ZnPc containing a mixture of differently sulfonated derivatives ($\text{ZnPcS}_{\text{mix}}$), Fig. 1. The photosensitizing effectiveness of MPc complexes is substantially reduced by aggregation of these complexes [6,7]. The excited triplet state is quenched in aggregated MPc complexes and the quantum yield for singlet oxygen production is decreased significantly. However, the degree of aggregation of the MPcS_{mix} species depends on the synthetic method and on the degree of sulfonation [8]. In this work we compare the photosensitizing abilities of ZnPc complexes towards the photodegradation of 4-Np. Even though there have been several reports on the use of MPc complexes for the photodegradation of chlorophenols [9–12], nitrophenols have not received much attention.

* Corresponding author. Fax: +27 46 622 5109.

E-mail address: t.nyokong@ru.ac.za (T. Nyokong).

Fig. 1. Molecular structure of ZnPcS_n and ZnPc(COOH)₈ complexes.

Scheme 1. Type II mechanism. Where subs-represents 4-nitrophenol. ISC is intersystem crossing.



Scheme 2. Type I mechanism.

2. Experimental

2.1. Materials

4-Nitrophenol (4-Np) was obtained from BDH. 4-Nitrocatechol (Aldrich) and hydroquinone (May and Baker) were of reagent grade, and were employed as standards for high performance liquid chromatography (HPLC). ZnPcS₄ was synthesized, purified and characterised according to Weber and Busch method [13]. ZnPcS_{mix}, was synthesised from ZnPc, using fuming sulphuric acid (30% SO₃) according to literature procedures [14]. ZnPc(COOH)₈ was prepared, purified and characterised according to the reported procedure [15]. ZnPc was either purchased from Aldrich or synthesized, purified and characterized using literature methods [16]. Ultra-pure water (Milli-Q Water System, Millipore Corp., Bedford, MA, USA) was used for all experiments and analyses. pH 8.2 phosphate buffer solutions, were prepared using reagent grade potassium dihydrogen orthophosphate (ACE) and dipotassium phosphate (PAL Chemicals).

2.2. Photochemical studies

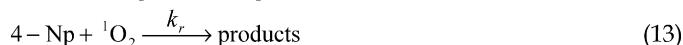
Irradiation in the visible region was carried out with a General Electric Quartz line lamp (300W). A 600 nm glass cut off filter (Schott) was used to filter off ultraviolet light, so that only the phthalocyanine Q band is irradiated, avoiding direct photodegradation of 4-Np by UV light. The light intensity was measured with a power meter (Lasermate/A) and was found to be 4.1×10^{16} photons s⁻¹ cm⁻². The pH of the buffer solutions were measured using the WTW pH 330/SET-1 pH meter. Experiments were performed where 4-Np and the ZnPc complexes were photolysed (in the visible region) individually, and in the presence of one another. The photocatalysis products were monitored in two ways: spectroscopically using Cary 500 UV-vis/NIR spectrophotometer or using high performance liquid chromatography (HPLC). We employed a Quad-Gradient Agilent 1100 series HPLC fitted with an analytical Prodigy 5 μm ODS (150 mm × 4.6 mm) column connected to a variable wavelength UV-vis detector. The UV-vis detector was set at 230 nm. The photocatalysis products were identified using HPLC by comparing retention times and by using fragmentation patterns as obtained from a liquid chromatograph connected to a mass spectrometer (LC/MS). Mass spectra were recorded with Finnigan LCQ-MS coupled with analytical Prodigy 5 μm ODS (150 mm × 4.6 mm) column. A mobile phase consisted of 70:30 methanol:water mixture.

2.3. Treatment of data

Quantum yields for the photodegradation of 4-Np ($\Phi_{4\text{-Np}}$) were determined from the initial linear part of the kinetic curve for photo-oxidation of 4-Np, using Eq. (10):

$$\Phi_{4\text{-Np}} = -\frac{(C_t - C_0)VN_A}{I_{\text{abs}}St} \quad (10)$$

where V is the reaction volume (4.5 cm³), t the irradiation time, N_A Avogadro's constant, S the irradiation area (1 cm²), and C_0 and C_t are 4-Np concentrations before and after irradiation, respectively. The extinction coefficient (ϵ) of 4-Np was determined to be 1.8×10^4 dm³ mol⁻¹ cm⁻¹ at 400 nm (pH 8.2) and used for calculation of 4-Np concentrations. I_{abs} from Eq. (10) is the overlap integral of light intensity of the radiation source and the light absorption of the sensitiser at 670 nm [17].



Scheme 3.

The rate constants of interest are those involved in singlet oxygen mechanism (type II) for the photodegradation of 4-Np. k_d , k_q and k_r are the rate constants for the decay of ${}^1\text{O}_2$ in water, “physical” quenching of ${}^1\text{O}_2$ by the substrate (4-Np) and formation of oxidation products, respectively, according to Scheme 3 (Eq. (11)–(13)).

Eq. (11)–(13) can be used to derive Eq. (14):

$$\Phi_{4\text{-Np}} = \Phi_{\Delta} \frac{k_r[4\text{-Np}]}{k_d + (k_r + k_q)[4\text{-Np}]} \quad (14)$$

where Φ_{Δ} is the singlet oxygen quantum yield.

Eq. (14) can then be rearranged to give Eq. (15):

$$\frac{1}{\Phi_{4\text{-Np}}} = \frac{1}{\Phi_{\Delta}} \left(\frac{k_r + k_q}{k_r} + \frac{k_d}{k_r[4\text{-Np}]} \right) \quad (15)$$

k_d , the singlet oxygen decay rate constant in water, can be calculated using Eq. (16):

$$k_d = \frac{1}{\tau_{\Delta}} \quad (16)$$

τ_{Δ} , the lifetime of singlet oxygen, is 3.09×10^{-6} s, therefore k_d is $3.22 \times 10^5 \text{ s}^{-1}$ [18].

From Eq. (15), a plot of $1/\Phi_{4\text{-Np}}$ versus $1/[4\text{-Np}]$ will result in the determination of k_r and $(k_r + k_q)$. The values of Φ_{Δ} for $\text{ZnPcS}_{\text{mix}}$, ZnPcS_4 and $\text{ZnPc}(\text{COOH})_8$ are 0.48, <0.01 and 0.52, respectively, Table 1, in pH 10 buffer [19], and were employed to calculate the rate constants.

3. Results and discussion

3.1. Optimization

Studies for the photocatalysed degradation of 4-Np were carried out at pH 8.2 since the pK_a value for 4-Np is 7.15 [20]. Fig. 2 shows the absorption spectral changes observed on photolysis of 4-Np in the presence of optimum $\text{ZnPcS}_{\text{mix}}$ concentration of 400 mg/L. A peak due to 4-Np was observed at 400 nm and it disappeared with time with the formation of peaks due to degradation products at ~ 280 nm. $\Phi_{4\text{-Np}}$ values were calculated from the data in Fig. 2 using Eq. (10), by determining the initial rate of disappearance of the 4-Np peak at 400 nm. The optimum amount of ZnPc complexes (using $\text{ZnPcS}_{\text{mix}}$ as an example) needed for the photodegradation of 4-Np was determined by plotting $\Phi_{4\text{-Np}}$ versus $[\text{ZnPcS}_{\text{mix}}]$, Fig. 3. The curve leveled off after 400 mg/L. Using the optimum $\text{ZnPcS}_{\text{mix}}$ concentration, the amount of 4-Np which gives the highest $\Phi_{4\text{-Np}}$ value was determined. Fig. 4 shows that the $\Phi_{4\text{-Np}}$ value peaked at $1.5 \times 10^{-4} \text{ mol L}^{-1}$ for 4-Np photocatalysed oxidation.

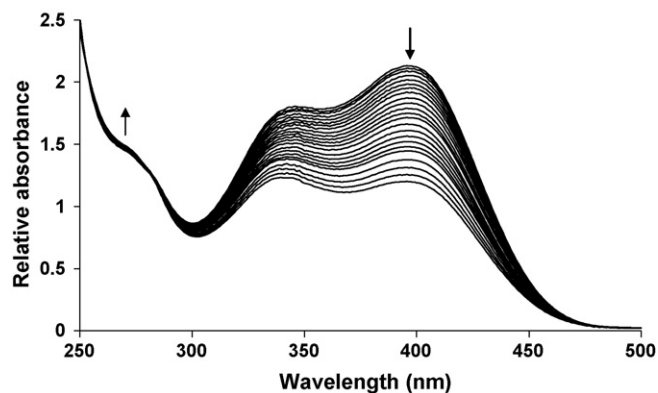


Fig. 2. Electronic absorption spectral changes observed during the photolysis of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ 4-Np in the presence of 400 mg dm^{-3} $\text{ZnPcS}_{\text{mix}}$ in pH 8.2 buffer solution.

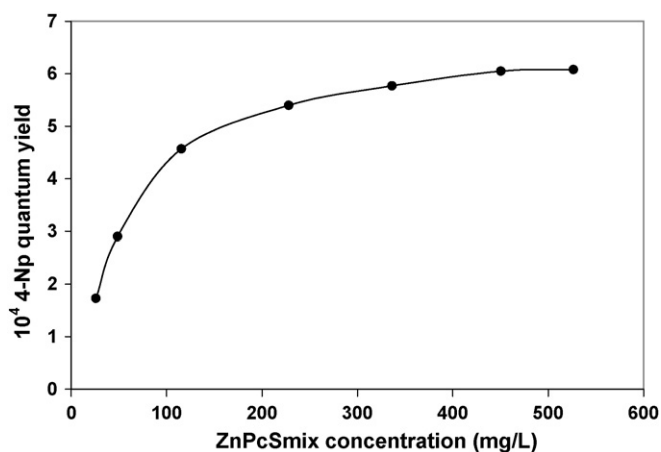


Fig. 3. Plot of $\Phi_{4\text{-Np}}$ vs. concentration of $\text{ZnPcS}_{\text{mix}}$ to determine the optimum concentration of $\text{ZnPcS}_{\text{mix}}$ for the phototransformation of 4-Np ($1.0 \times 10^{-4} \text{ mol/L}$); pH 8.2.

Experiments were performed whereby 4-Np was photolysed (visible light) in the absence of the photosensitizer. No spectral changes (or changes in HPLC traces) were observed showing that the transformation of 4-Np occurred only through photocatalysis under visible light radiation.

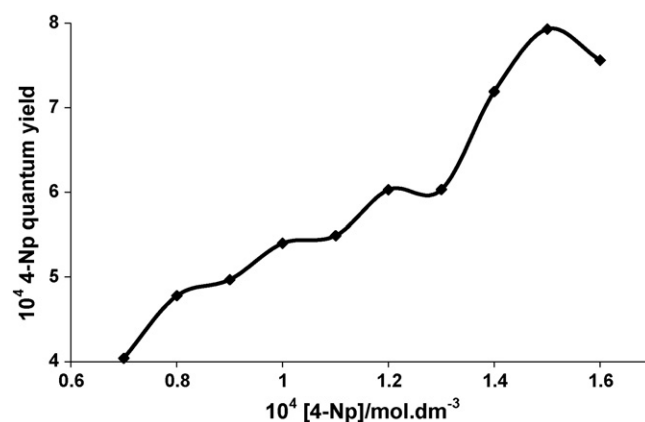


Fig. 4. Plot of $\Phi_{4\text{-Np}}$ vs. concentration of 4-Np for its phototransformation in the presence of $\text{ZnPcS}_{\text{mix}}$ (400 mg/L); pH 8.2.

Table 1

Photosensitization data for 4-Np transformation in the presence of the various sensitizers (400 or 200 mg L⁻¹) under visible light irradiation (for 10 min). pH 8.2; [4-Np] = 1.0 × 10⁻⁴ mol L⁻¹

| ZnPc complex | Φ_{4-Np} (400 mg/L MPC) | Φ_{4-Np} (200 mg/L MPC) | Φ_{Δ}^a | Degradation of MPC complex (%) | Degree of aggregation (%) |
|-------------------------|------------------------------|------------------------------|-------------------|--------------------------------|---------------------------|
| ZnPcS _{mix} | 7.9 × 10 ⁻⁴ | 7.4 × 10 ⁻⁴ | 0.48 | 15 | 49 |
| ZnPcS ₄ | 1.5 × 10 ⁻⁴ | 1.2 × 10 ⁻⁴ | <0.01 | 2 | 78 |
| ZnPc(COOH) ₈ | 6.5 × 10 ⁻³ | 1.8 × 10 ⁻³ | 0.52 | 23 | 29 |

^a From Ref. [12] in pH 10 buffer.

3.2. Comparison of the photocatalytic activities of the ZnPc sensitizers

Fig. 5 shows the decrease of the concentration of 4-Np with time during irradiation in the presence of the various photosensitizers at pH 8.2. The disappearance of 4-Np was monitored with UV–vis spectrophotometer. The results show that photooxidation of 4-Np occurred faster when ZnPc(COOH)₈ was used as the sensitizer. ZnPcS₄ showed the least activity towards the photooxidation of 4-Np. Values of quantum yields, Φ_{4-Np} , for 4-Np photosensitized oxidation at the concentration of the photosensitizer of 400 mg L⁻¹ and 1.0 × 10⁻⁴ mol L⁻¹ of 4-Np were 7.9 × 10⁻⁴, 1.5 × 10⁻⁴ and 6.5 × 10⁻³ for ZnPcS_{mix}, ZnPcS₄ and ZnPc(COOH)₈, respectively (Table 1). Similarly, the values of Φ_{4-Np} for 4-Np photosensitized oxidation at lower concentrations of the catalyst (200 mg/L) and 1.0 × 10⁻³ mol L⁻¹ 4-Np were 7.4 × 10⁻⁴, 1.2 × 10⁻⁴ and 1.8 × 10⁻³ for ZnPcS_{mix}, ZnPcS₄ and ZnPc(COOH)₈, respectively (Table 1). Two main factors determine photosensitizer activity: efficiency of singlet oxygen sensitization and sensitizer photodegradation. ZnPc(COOH)₈ has the largest singlet oxygen quantum yield (Table 1) hence it is the best photocatalyst. In terms of aggregation, this complex was aggregated at the concentrations employed in this work, even though it is known to be less aggregated than ZnPcS₄ and ZnPcS_{mix} [19]. ZnPcS_{mix} has a slightly lower singlet oxygen quantum yield compared to ZnPc(COOH)₈, hence a lower photocatalytic activity. Because of the very low rate of photodegradation of 4-Np in the presence of ZnPcS₄, this complex was not employed any further for the study of rate constants. The reason for the low activity of this complex is its low singlet oxygen yield, Table 1.

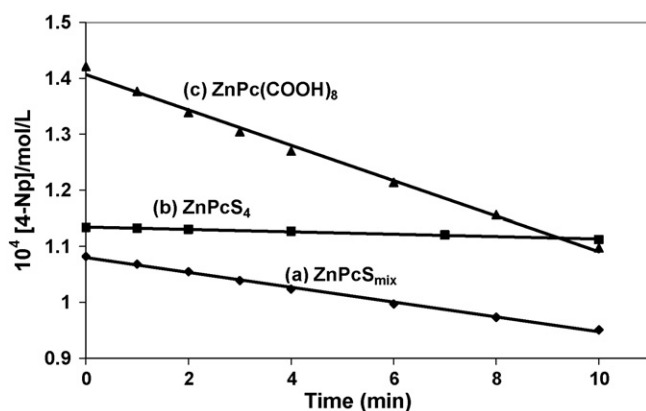


Fig. 5. Plot of [4-Np] vs. time for: (a) ZnPcS_{mix}, (b) ZnPcS₄ and (c) ZnPc(COOH)₈; [MPC] = 200 mg L⁻¹.

MPCs_{mix} complexes containing a mixture of sulfo (mono-, di-, tri- and tetra) substituents are important to study (as mixtures) since AlPcS_{mix} for example, is already in use as a photosensitizer for medical purposes (for photodynamic therapy, PDT [21]). It is known [8] that MPCs_{mix} preparations consisting of the least number of isomeric species show a greater tendency to form aggregates, whereas the more complex preparations consisting of a higher number of differently substituted compounds show less aggregation. The degree of aggregation increases with lipophilicity [8]. HPLC chromatogram for ZnPcS_{mix} using an analytical column is shown in Fig. 6. It is expected that the most highly sulphonated component will be the first to be eluted from the chromatographic column, and so gives the lowest retention time and that the least sulphonated fractions give the highest retention times [22]. Fig. 6 shows that the most intense chromatogram peaks are at low retention times, suggesting that ZnPcS_{mix} consist mainly of the more sulfonated derivatives. This is contrary to previous HPLC analysis which showed ZnPcS_{mix} to consist of the less sulphonated fractions [23,24]. This goes to confirm the observation that the composition of the prepared MPCs_{mix} complexes may vary from batch to batch.

The formation of aggregates in sulfophthalocyanines is characterized by broadening in the visible region of the spectra and the presence of a low energy band near 630 nm due to sandwich type dimer formation. At the concentration employed for photocatalysis in this work, all the sensitizers were aggregated. The degree of aggregation was determined from the increase in the Q band intensity in the presence of Triton X-100, and tabulated in Table 1. Fig. 7 shows that adequate monomerization was obtained for ZnPcS₄ and ZnPcS_{mix}, but not for ZnPc(COOH)₈ on addition of Triton X-100. Even addition of DMSO did not disaggregate the latter. Thus the percent aggregation values in Table 1 for ZnPc(COOH)₈ are not an accurate representation.

The fate of the photocatalyst is important. A stable photocatalyst which also results in high degradation rate of 4-Np

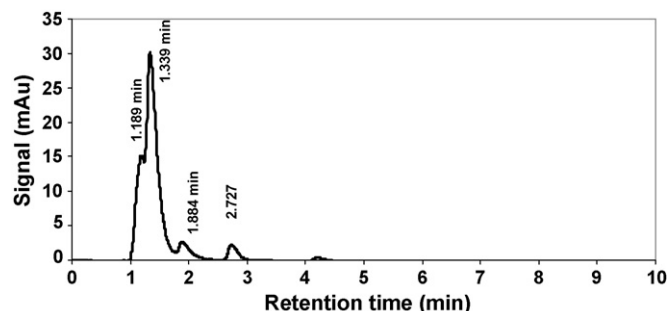


Fig. 6. HPLC chromatogram for ZnPcS_{mix}.

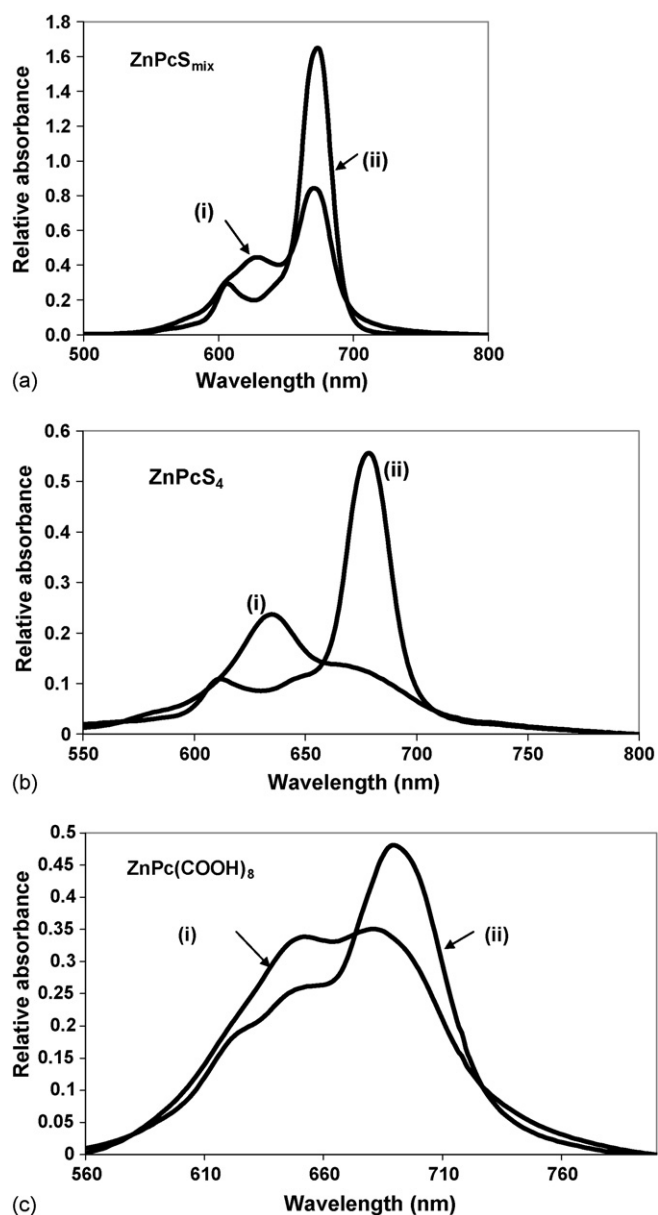


Fig. 7. Spectral changes observed on addition of Triton X-100 to solutions of: (a) $\text{ZnPcS}_{\text{mix}}$, (b) ZnPcS_4 and (c) $\text{ZnPc}(\text{COOH})_8$. (i) Buffer only and (ii) buffer and Triton X-100.

would be preferred. Fig. 8 shows the spectroscopic changes observed for $\text{ZnPcS}_{\text{mix}}$, ZnPcS_4 and $\text{ZnPc}(\text{COOH})_8$ during photocatalytic oxidation of 4-Np. ZnPcS_4 showed good stability during the catalysis, (Fig. 8a). ZnPcS_4 showed minimal degradation (only $\sim 2\%$, Table 1). However due to the minimal value of singlet oxygen quantum yield, ZnPcS_4 was not an efficient photocatalyst. As has been reported before [25] for photooxidation of 4-chlorophenol (4-Cp), $\text{ZnPc}(\text{COOH})_8$ showed significant degradation during the photolysis process in this work. However, this complex gave the best photocatalytic activity for 4-Np compared to the other two. This is unlike for the photocatalysis of 4-Cp [25] where it gave poor catalytic activity compared to $\text{ZnPcS}_{\text{mix}}$, and the poor catalytic activity was attributed to high degree of degradation. Fig. 8 shows that during degrada-

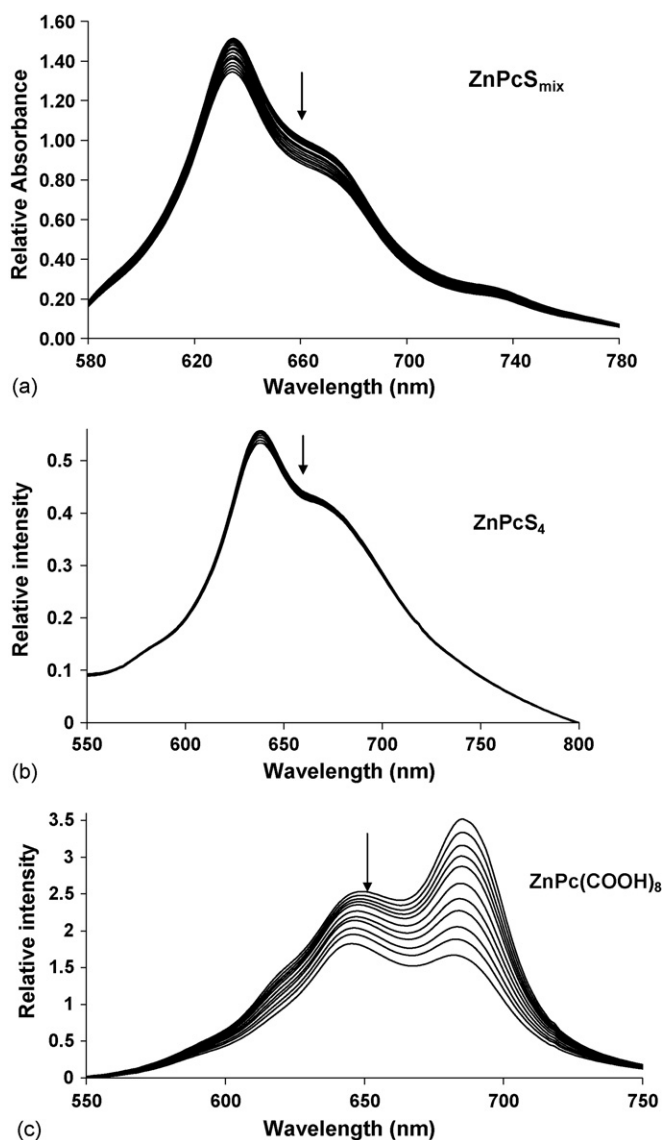


Fig. 8. Spectral changes observed for: (a) $\text{ZnPcS}_{\text{mix}}$, (b) ZnPcS_4 and (c) $\text{ZnPc}(\text{COOH})_8$ during the photocatalytic oxidation of 1.0×10^{-4} mol/L 4-Np; pH 8.2.

tion of $\text{ZnPc}(\text{COOH})_8$, the monomer peak at 684 nm decreases faster than the dimer peak at 648 nm. It is expected that it is the monomer which is involved in photocatalysis, thus the monomer is used up at the expense of the aggregate. Increased aggregation could also result from the decarboxylation of the $\text{ZnPc}(\text{COOH})_8$. However this would result in unsymmetrically substituted derivatives hence an additional splitting of the Q band, which was not observed. Thus we believe decarboxylation is not likely. Phthalocyanine molecules in general photodegrade oxidatively via attack by the singlet oxygen they generate.

3.3. Determination of rate constants using $\text{ZnPcS}_{\text{mix}}$ and $\text{ZnPc}(\text{COOH})_8$

Fig. 9 shows the linear plot of $1/\Phi_{4\text{-Np}}$ versus $1/[4\text{-Np}]$, using $\text{ZnPcS}_{\text{mix}}$ and $\text{ZnPc}(\text{COOH})_8$ sensitizers. From Eq. (15),

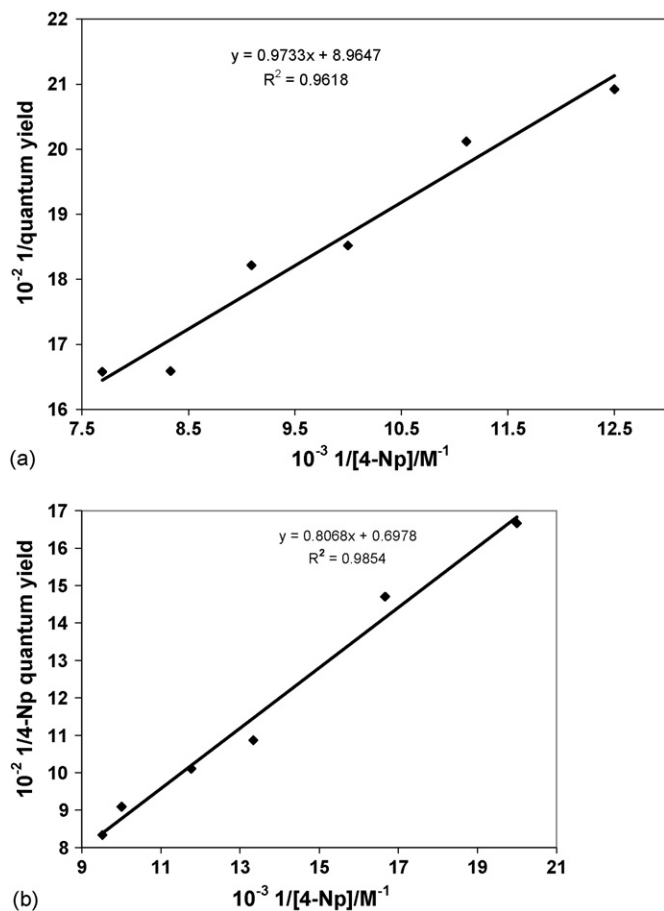


Fig. 9. Plot of $1/\Phi_{4-Np}$ vs. $1/[4-Np]$ for the phototransformation of 4-Np in the presence of: (a) $ZnPcS_{mix}$ (400 mg dm^{-3}) and (b) $ZnPc(COOH)_8$ (200 mg dm^{-3}); pH 8.2.

the slope is equal to $k_d/\Phi_{\Delta}k_r$, where $k_d = 3.22 \times 10^5 \text{ s}^{-1}$ (Eq. (16)) and $\Phi_{\Delta} = 0.48$, therefore $k_r = 0.67 \times 10^6 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$. The intercept ($(k_q + k_r)/\Phi_{\Delta}k_r$) in Fig. 9a = 896.5. Using the values of Φ_{Δ} and k_r (0.48 and $0.67 \times 10^6 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, respectively), $(k_q + k_r)$ was calculated to be $2.9 \times 10^8 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$. For $ZnPc(COOH)_8$, the values of $(k_q + k_r)$ and k_r were $2.8 \times 10^8 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and $7.7 \times 10^6 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, respectively. The values of $(k_q + k_r)$ for both $ZnPcS_{mix}$ and $ZnPc(COOH)_8$ are 400 and 40 times greater than k_r (the rate constant for photo-oxidation alone), respectively, which indicates that most of the singlet oxygen that is generated is scavenged by a quenching process. 4-Np therefore quenches singlet oxygen faster than it reacts with singlet oxygen. This situation has been observed for many phenols [1]. The reported k_r and $(k_q + k_r)$ values for the phototransformation of 4-chlorophenol (4-Cp) in the presence of $ZnPcS_{mix}$ were $2.8 \times 10^8 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and $12.5 \times 10^8 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, respectively [25,26]. Thus (4-Cp) also quenches singlet oxygen faster than it reacts with singlet oxygen, as $(k_q + k_r)$ is five times greater than k_r . However it is evident from comparing the k_r values obtained for 4-Cp and 4-Np that 4-Cp reacts with singlet oxygen to a greater extent than 4-Np.

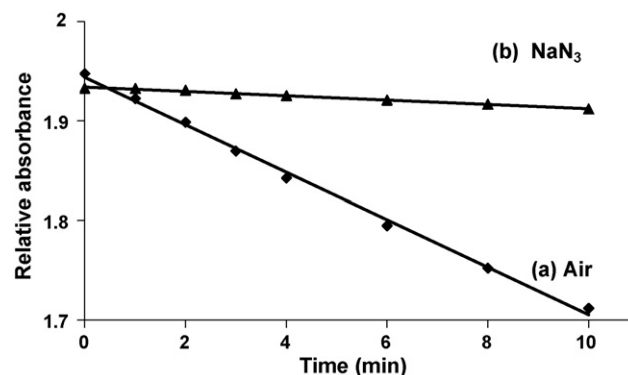


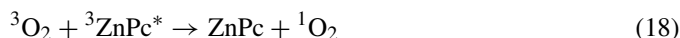
Fig. 10. Effects of addition of sodium azide (an oxygen scavenger) on the rate 4-Np degradation in air: (a) no NaN_3 ; (b) NaN_3 added. Catalyst = $ZnPcS_{mix}$.

3.4. The mechanism for the photodegradation of 4-Np

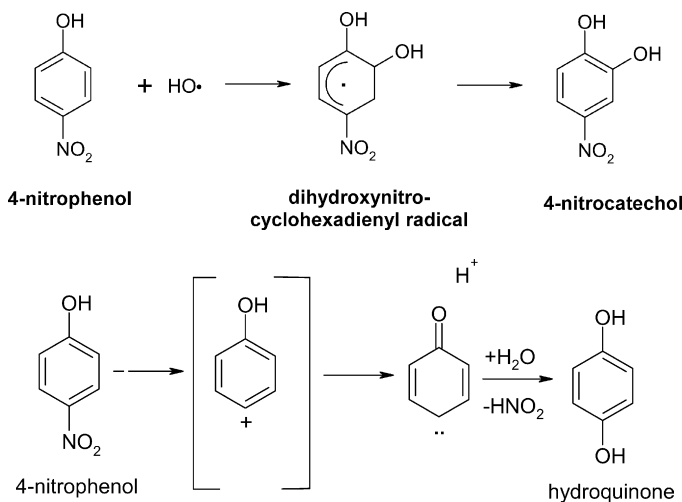
The products for the photodegradation of 4-Np were determined either by LC/MS, or comparison of retention times of standards: 4-nitrocatechol and hydroquinone.

The involvement of singlet oxygen in the photocatalysis mechanism was confirmed by performing photocatalysis experiments in air and in the presence of NaN_3 , as NaN_3 is an oxygen-scavenger. Fig. 10 shows faster kinetics for 4-Np in air hence confirming the involvement of oxygen. No spectral changes were observed on addition of NaN_3 to solutions of $ZnPcS_{mix}$ hence confirming that the observed changes are due to singlet oxygen not deactivation of the catalyst.

The proposed mechanism for the photodegradation of 4-Np in the presence of ZnPc photosensitizers is as follows:



Possible mechanisms for the formation of 4-nitrocatechol and hydroquinone are as follows [1].



4. Conclusions

Water soluble phthalocyanine complexes $\text{ZnPcS}_{\text{mix}}$, ZnPcS_4 and $\text{ZnPc}(\text{COOH})_8$ have been employed for the photocatalytic degradation of 4-Np. $\text{ZnPcS}_{\text{mix}}$ is the most effective catalyst in terms of the rate of 4-Np degradation and the stability of the catalyst. $\text{ZnPc}(\text{COOH})_8$ degrades readily during the catalysis. But it has a higher quantum yield ($\Phi_{4\text{-Np}}$) for 4-Np degradation than the rest of the complexes. The $\Phi_{4\text{-Np}}$ values were closely related to the singlet oxygen quantum yields Φ_{Δ} and hence aggregation. The products of photodegradation were hydroquinone and 4-nitrocatechol.

Acknowledgements

This work was supported by Rhodes University and National Research Foundation (NRF, Gun = 2053657) in South Africa.

References

- [1] A. Di Paola, V. Augugliaro, L. Palmisano, G. Pantaleo, E. Savinov, J. Photochem. Photobiol. A: Chem. 155 (2003) 207–214.
- [2] US Environmental Protection Agency, Nitrophenols, Ambient Water Quality, Washington, DC, 1980.
- [3] R. Bonnett, Chem. Soc. Rev. 24 (1995) 19–33.
- [4] R. Bonnett, in: D. Phillips, P. O'Brein, S. Roberts (Eds.), Chemical Aspects of Photodynamic Therapy. Advanced Chemistry Texts, vol. 1, Gordon and Breach, Germany, 2000.
- [5] I. Rosenthal, E. Ben-Hur, Int. J. Radiat. Biol. 67 (1995) 85.
- [6] V. Iliev, V. Alexiev, L. Bilyarska, J. Mol. Catal. A: Chem. 137 (1999) 15.
- [7] E.A. Lukyanets, J. Porphyrins Phthalocyanines 3 (1999) 424.
- [8] R. Edrei, V. Gottfried, J.E. Van Lier, S. Kimel, J. Porphyrins Phthalocyanines 2 (1998) 191.
- [9] R. Gerdes, D. Wöhrle, W. Spiller, G. Schneider, G. Schnurpfeil, G. Schulz-Ekloff, J. Photochem. Photobiol. A: Chem. 111 (1997) 65.
- [10] K. Lang, D.M. Wagnerová, J. Brodilová, J. Photochem. Photobiol. A: Chem. 72 (1993) 9.
- [11] K. Ozoemena, N. Kuznetsova, T. Nyokong, J. Mol. Catal. A: Chem. 176 (2001) 29.
- [12] B. Agboola, K.I. Ozoemena, T. Nyokong, J. Mol. Catal. A: Chem. 248 (2006) 84.
- [13] J.H. Weber, D.H. Busch, Inorg. Chem. 4 (1965) 469.
- [14] M. Ambroz, A. Beeby, A.J. MacRobert, M.S.C. Simpson, R.K. Svendsen, D. Phillips, J. Photochem. Photobiol. B: Biol. 9 (1991) 87.
- [15] K. Sakamoto, E. Ohno, Prog. Org. Coat. 31 (1997) 139.
- [16] H. Tomoda, S. Saito, S. Shiraishi, Chem. Lett. 12 (1983) 313.
- [17] I. Seotsanyana-Mokhosi, N. Kuznetsova, T. Nyokong, J. Photochem. Photobiol. A: Chem. 140 (2001) 215.
- [18] S. Egorov, V. Kamalov, N. Koroteev, A. Kransovsky, B. Toleutaev, S. Zinukoz, Chem. Phys. Lett. 163 (1989) 421.
- [19] K. Ozoemena, N. Kuznetsova, T. Nyokong, J. Photochem. Photobiol. A: Chem. 139 (2001) 217.
- [20] M.M. Fickling, A. Fischer, B.R. Mann, J. Packer, J. Vaughan, J. Am. Chem. Soc. 81 (1959) 4226.
- [21] V.V. Sokolov, E.F. Stranadko, N.N. Zharkova, R.I. Iakubovskaia, E.V. Filonenko, T.A. Voprosy, Onkologii 41 (1995) 134.
- [22] M. Ambroz, A. Beeby, A.J. McRobert, M.S.C. Simpson, R.K. Svendsen, D. Phillips, J. Photochem. Photobiol. B: Biol. 9 (1991) 87.
- [23] A.O. Ogunsipe, T. Nyokong, J. Photochem. Photobiol. A: Chem. 173 (2005) 211.
- [24] A.O. Ogunsipe, T. Nyokong, Photochem. Photobiol. Sci. 4 (2005) 510.
- [25] K. Ozoemena, N. Kuznetsova, T. Nyokong, J. Photochem. Photobiol. A: Chem. 139 (2001) 217.
- [26] M.J. Thomas, C.S. Foote, Photochem. Photobiol. 27 (1978) 683.