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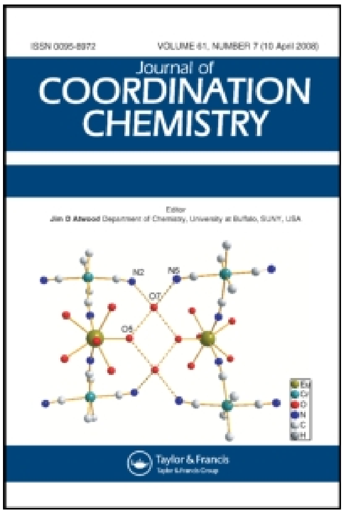

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Photocatalytic transformation of 4-nitrophenol in aqueous media using suspended, water-insoluble metallophthalocyanine complexes

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Unsubstituted magnesium (MgPc), zinc (ZnPc) and chloroaluminium (ClAlPc) phthalocyanine complexes and the ring substituted zinc tetranitro ($ZnPc(NO_2)_4$), zinc tetraamino ($ZnPc(NH_2)_4$), zinc hexadecafluoro ($ZnPcF_{16}$) and zinc hexadecachloro ($ZnPcCl_{16}$), phthalocyanine complexes are employed as photocatalysts for the heterogeneous transformation of 4-nitrophenol (4-Np) to fumaric acid and 4-nitrocatechol. ClAlPc is the best catalyst, with 89 ± 8% degradation of 4-Np after 100 min. The least effective catalysts were $ZnPcCl_{16}$ and MgPc.

Keywords: Nitrophenol; Photocatalysis; Heterogeneous; Zinc phthalocyanine; Magnesium phthalocyanine; Aluminium phthalocyanine

1. Introduction

The presence of phenols in waste effluent streams and runoff from agricultural land is of growing concern due to their relatively high toxicity. Nitrophenols are of special interest due to their inclusion as priority toxic pollutants by agencies such as the United States Environmental Protection Agency [1]. Their removal from groundwater and surface water is hindered due to their high stability and solubility in water as well as their resistance to traditional methods of water purification [2], including microbial degradation and chemical oxidation. These two methods are disadvantageous as microbial degradation of nitrophenols is time-consuming and chemical oxidation is only feasible at high pollutant concentrations [2, 3]. 4-Nitrophenol (4-Np) was selected as the substrate for this study as it is more toxic than the other mononitrophenols and is produced in the highest quantities worldwide [1]. 4-Np is employed in the synthesis of pharmaceutical drugs, pesticides, such as nitrofen and methyl parathion, and dyes to darken leather. Consequently, the degradation of pesticides, such as nitrofen and methyl parathion, results in the release of 4-Np into the environment [1].

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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 state of the MPc sensitizer (${}^3\mathrm{MPc}^*$) with ground state oxygen (${}^3\mathrm{O}_2, {}^3\Sigma_g^-$) to produce active singlet oxygen (${}^1\mathrm{O}_2, {}^1\Delta_g$), through the so-called Type II mechanism. This occurs via triplet-triplet energy transfer, equations (1)–(3), scheme 1 [4].

The other possible route involves participation of a superoxide radical through the so-called Type I mechanism (equations (4)–(9), scheme 2 [5–7]). The superoxide species is unstable and reactive, resulting in generation of hydroxyl radicals by the subsequent chain reactions.

Non-transition MPcs (particularly those containing Al(III) and Zn(II)) are effective for photocatalysis since they produce high triplet quantum yields, leading to high quantum yields of singlet oxygen (essential for Type II mechanism) [8]. The degradation of 4-Np in the presence of water-soluble MPcs has been reported; however, the homogeneous photocatalysis of 4-Np poses a problem, as the photocatalysts are not easily recovered for reuse [9]. Hence, the degradation of 4-Np in the presence of water-insoluble phthalocyanines is under investigation. The phthalocyanine complexes that are employed in this study include unsubstituted magnesium phthalocyanine (MgPc), zinc phthalocyanine (ZnPc) and aluminium phthalocyanine (ClAlPc). The peripherally-substituted phthalocyanines that are employed as photocatalysts include zinc tetranitrophthalocyanine ($\mathrm{ZnPc(NO_2)_4}$), zinc tetraaminophthalocyanine ($\mathrm{ZnPc(NH_2)_4}$), zinc hexadecafluorophthalocyanine ($\mathrm{ZnPcF_{16}}$) and zinc hexadecachlorophthalocyanine ($\mathrm{ZnPcCl_{16}}$), figure 1.

$$\mathrm{MPc} \xrightarrow{h\nu} {}^1\mathrm{MPc}^* \xrightarrow{\mathrm{ISC}} {}^3\mathrm{MPc}^* \tag{1}$$

$$ {}^3\mathrm{MPc}^* + {}^3\mathrm{O}_2({}^3\Sigma_g^-) \longrightarrow \mathrm{MPc} + {}^1\mathrm{O}_2({}^1\Delta_g) \tag{2}$$

$$ {}^1\mathrm{O}_2({}^1\Delta_g) + \mathrm{Subs} \longrightarrow \text{Oxidation Products} \tag{3}$$

Scheme 1. Type II mechanism, where Subs is 4-Np and ISC is intersystem crossing.

$$ {}^3\mathrm{MPc}^* + \mathrm{O}_2 \longrightarrow \mathrm{MPc}^{+\bullet} + \mathrm{O}_2^{-\bullet} \tag{4}$$

$$ {}^3\mathrm{MPc}^* + \mathrm{Subs} \longrightarrow \mathrm{MPc}^{-\bullet} + \mathrm{Subs}^{+\bullet} \tag{5}$$

$$ \mathrm{MPc}^{-\bullet} + \mathrm{O}_2 \longrightarrow \mathrm{MPc} + \mathrm{O}_2^{-\bullet} \tag{6}$$

$$ \mathrm{O}_2^{-\bullet} + \mathrm{H_2O} \rightarrow \mathrm{OH}^- + \mathrm{HO}_2^\bullet \tag{7}$$

$$ \mathrm{HO}_2^\bullet + \mathrm{HO}_2^\bullet \rightarrow \mathrm{H_2O_2} + \mathrm{O}_2 \tag{8}$$

$$ \mathrm{H_2O_2} + \mathrm{O}_2^{-\bullet} \rightarrow \mathrm{OH}^\bullet + \mathrm{OH}^- + \mathrm{O}_2 \tag{9}$$

Scheme 2. Type I mechanism, Subs = 4-Np.

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The photosensitizing effectiveness of MPc complexes is substantially reduced by aggregation [10, 11]. The excited triplet state is quenched in aggregated MPc complexes and the triplet lifetime (and hence singlet oxygen quantum yield) is decreased significantly. In this work we compare the photosensitizing abilities of the aforementioned phthalocyanine 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 [12–17], nitrophenols have not received much attention, particularly their degradation in the presence of heterogeneous phthalocyanine photocatalysts.

2. Experimental

2.1. *Materials and reagents*

4-Np was obtained from BDH Chemical Co., UK. *N*,*N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were purchased from Merck and Riedel-de Haën, respectively. Tetrasodium α–α'-(anthracene-9,10-diyl) bis(methylmalonate) (ADMA) was purchased from Fluka. DABCO (1,4-diazabicyclo[2.2.2]octane) was obtained from Aldrich. 4-Nitrocatechol (Aldrich), 1,4-benzoquinone (Aldrich) and hydroquinone (May & Baker) were employed as high performance liquid chromatography (HPLC) standards. All reagents were used as received.

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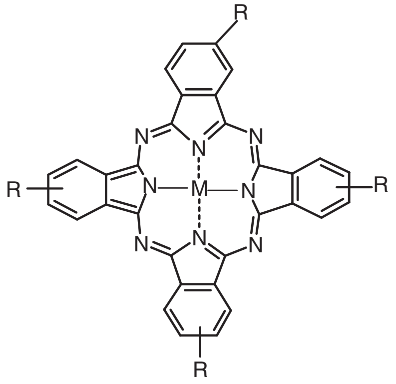
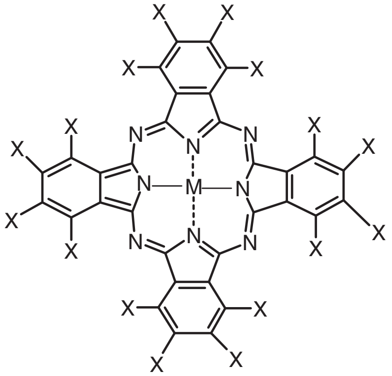


Complex	Ring substituent R =
MgPc	H
ClAlPc	H
ZnPc	H
$ZnPc(NO_2)_4$	NO_2
$ZnPc(NH_2)_4$	NH_2



$ZnPcF_{16}$: (X = F)

$ZnPcCl_{16}$: (X = Cl)

Figure 1. Molecular structure of the phthalocyanines studied.

The unsubstituted phthalocyanine complexes, MgPc, [18], ZnPc [18] and ClAlPc [19] were synthesized and purified according to literature methods. $ZnPc(NO_2)_4$ synthesis was based on methods described by Achar *et al.* [20] and Metz *et al.* [21]. $ZnPc(NH_2)_4$ was obtained by reducing $ZnPc(NO_2)_4$ using sodium sulphide nonahydrate [20]. $ZnPcF_{16}$ was synthesized, purified and characterized according to the reported procedure [22]. The synthesis of $ZnPcCl_{16}$ is based on methods described by Golovin *et al.* [23] and Decréau *et al.* [24]. All the complexes are well known and gave satisfactory spectroscopic analyses in agreement with the literature. The synthesis resulted in powdered MPc which were suspended in aqueous solutions for photocatalytic studies. No attempt was made to make the compounds into granular material.

A phosphate buffer (pH 9) used for the photocatalysis of 4-Np was prepared using reagent grade potassium dihygrogen orthophosphate (ACE Chemicals) and dipotassium hydrogen phosphate (PAL Chemicals). The pKa of 4-Np is 7.15 [25], therefore 4-Np is present as the phenolate ion at pH 9, aiding substrate oxidation [13].

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2.2. *Photochemical studies*

Irradiation in the visible region was achieved through the photochemical set-up consisting of a General Electric Quartz line lamp (300 W), a 600 nm glass cut off filter (Schott) used to filter off ultraviolet light and a glass photoreactor with a capacity of 40 mL. The photoreactor consists of three ports to allow for the introduction of oxygen, addition of the 4-Np solution, addition of the photocatalyst and sampling during photocatalysis. The reactor is surrounded by a water jacket to ensure that the contents of the photoreactor remain cool and aid in filtering off ultraviolet light. The solution, consisting of the photocatalyst (suspended as powdered solid) and 10 mL of $1 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$ 4-Np was saturated with oxygen prior to photodegradation of the solution. A power meter (Lasermate/A) was used to measure the intensity of light which was determined to be 5×10^{16} photons $\mathrm{s^{-1}\,cm^{-2}}$.

The pH of the phosphate buffer solution was measured using a WTW pH 330/SET-1 pH meter.

A Cary 500 UV–Vis/NIR spectrophotometer was used to characterize the MPcs and determine the mechanism of 4-Np degradation.

The degree to which the phthalocyanine complexes degrade 4-Np was determined using HPLC. A Quad-Gradient Agilent 1100 series HPLC fitted with an analytical Prodigy 5 µm ODS (150 mm × 4.6 mm) column was employed. The HPLC was fitted with a variable wavelength UV-vis detector set at 210 nm and 400 nm. The mobile phase consisted of 85 : 15 water : acetonitrile. Samples extracted from the 4-Np solution were filtered before analysis and 50 µL of the extracted sample was injected onto the HPLC column.

The degradation products formed after photolysis of 4-Np were identified using HPLC (by spiking with standards) and liquid chromatography coupled with mass spectrometry (LC/MS). Mass spectra were recorded with a Finnigan LCQ-MS by direct injection. The mobile phase for the HPLC consisted of a mixture of 85 : 15 water : acetonitrile.

Triplet lifetimes (τ_T) were obtained using a Nd-YAG laser providing 400 mJ, 90 ns of light at 10 Hz, pumping a Lambda-Physik FL 3002 dye laser. A 300 W xenon arc lamp (Thermo Oriel) provided the analyzing light. Kinetic curves were averaged over 256 laser pulses using a Tektronix TDS 360 digital oscilloscope. The τ_T values were obtained by fitting an exponential curve to the kinetic data using ORIGIN Pro 6.0.

3. Results and discussion

3.1. *Characterization of photocatalysts*

The triplet lifetimes were determined for the MPcs in DMSO (table 1). Aggregation is not desired in MPc complexes since it results in reduced τ_T values. Triplet lifetimes and triplet quantum yields provide an indication of the MPcs' abilities to convert ground state oxygen ($^3O_2, ^3\Sigma_g^-$) to singlet state oxygen ($^1O_2, ^1\Delta_g$) [26]. The higher the τ_T values the higher the probability of energy transfer from triplet state MPc to triplet oxygen. Even though the triplet lifetime values were determined in solution (DMSO), and the MPc complexes are in the solid state for the photocatalyses, they give an indication of the relative lifetimes of the complexes.

The trend in triplet lifetime values for the selected phthalocyanine complexes is as follows: $ClAlPc > MgPc > ZnPc > ZnPcF_{16} = ZnPc(NH_2)_4 > ZnPc(NO_2)_4 > ZnPcCl_{16}$. The high triplet lifetimes obtained for ZnPc, MgPc and ClAlPc complexes can be attributed to their monomeric character in DMSO (figure 2). The substituted phthalocyanines, excluding $ZnPc(NH_2)_4$, are highly aggregated in DMSO (figure 3). The relatively low triplet lifetime obtained for $ZnPcF_{16}$, compared to that obtained for ZnPc, can be accounted for by considering the "heavy-atom" effect of fluorines, which is expected to increase triplet quantum yields but lower triplet lifetime values [8]. The "heavy-atom" effect of $ZnPcCl_{16}$ leads to its inability to remain in the excited triplet state for a measurable amount of time.

Table 1. Triplet lifetime (τ_T) values obtained for the selected phthalocyanine complexes in DMSO unless otherwise stated.

Photocatalyst	τ_T (μs)	Φ_Δ[a]
MgPc	400 ± 4.3	0.40 [5][a]
ZnPc	320 ± 5.6	0.67 [26,27]
ClAlPc	470 ± 3.5	0.29 [26]
$ZnPc(NO_2)_4$	60 ± 2.7	0.11 [27]
$ZnPc(NH_2)_4$	150 ± 2.9	0.11 [27]
$ZnPcF_{16}$	150 ± 8.1	0.13 [26][b]
$ZnPcCl_{16}$	Not detected	–

[a] Singlet oxygen quantum (Φ_Δ) represents the amount of singlet oxygen generated per quanta of light. References in brackets.

[b] Solvent = acetone.

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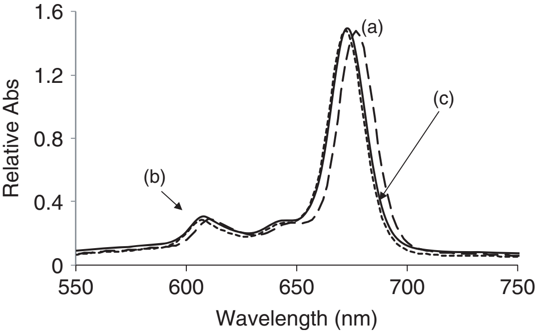

Figure 2. Spectra obtained for the unsubstituted phthalocyanine complexes in DMSO. (a) ClAlPc (7.9×10^{-6} mol dm^{-3}), (b) MgPc (1.9×10^{-5} mol dm^{-3}) and (c) ZnPc (6.5×10^{-6} mol dm^{-3}).

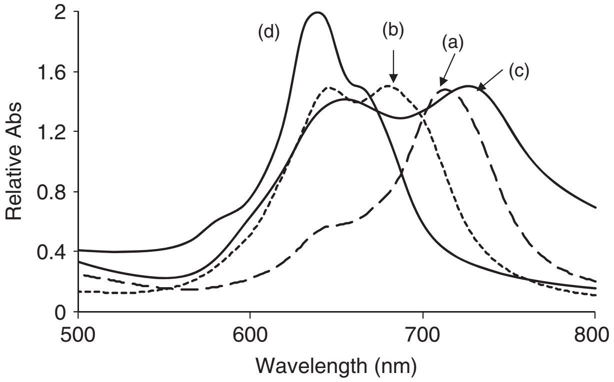

Figure 3. Spectra obtained for the substituted zinc phthalocyanine complexes in DMSO. (a) $ZnPc(NH_2)_4$, (b) $ZnPc(NO_2)_4$, (c) $ZnPcCl_{16}$ and (d) $ZnPcF_{16}$.

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3.2. *Effects of catalyst concentration*

Figure 4 shows the HPLC traces for 4-Np degradation following photolysis for 100 min in the presence of suspended ZnPc (as an example) followed by filtering of the solution; the inset shows the HPLC trace for 4-Np before photolysis. The products were identified by LC-MS and by spiking of the HPLC peaks with standards. The final products were 4-nitrocatechol and fumaric acid, with the latter being the major product. Benzoquinone and hydroquinone were observed as intermediates in that they were formed initially and their peaks decreased with time as the peaks due to fumaric acid and 4-nitrocatechol increased. Mass spectral peaks were observed at $m/z = 117$ amu (M + 1) for fumaric acid and $m/z = 155$ amu (M + 1) for 4-nitrocatechol.

The oxidation of 4-Np was performed by maintaining 4-Np at a constant concentration (1×10^{-5} mol dm^{-3}) and varying loading of the catalyst (ZnPc in this instance). After 100 min of irradiation with visible light, the solution was filtered and analyzed using the HPLC system described above. A linear increase in the formation of the major degradation product (i.e. fumaric acid) was observed on plotting the average peak height of the degradation product vs. the concentration of

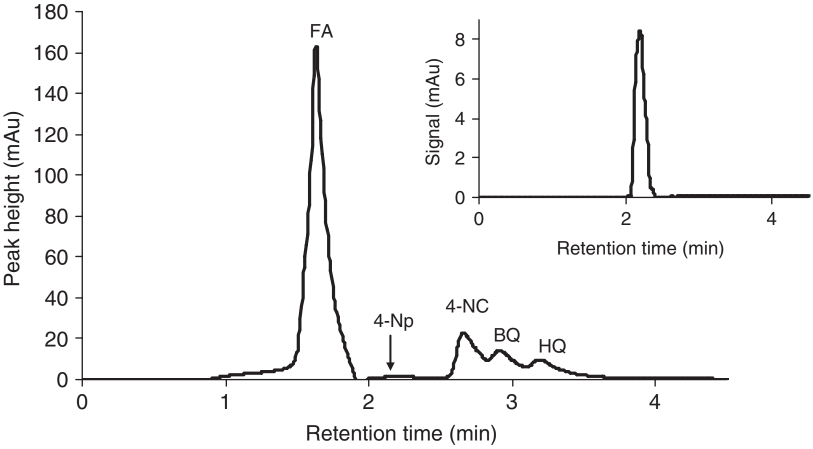

Figure 4. HPLC chromatogram of the reaction mixture after photocatalysis of 4-Np in the presence of $ZnPc(NH_2)_4$ for 100 min. ($[4\text{-Np}] = 1.0 \times 10^{-5}\,\text{mol dm}^{-3}$, pH = 9, FA = fumaric acid, 4-NC = 4-nitrocatechol, BQ = 1,4-benzoquinone, HQ = hydroquinone). Inset: HPLC trace for 4-Np before photolysis.

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ZnPc (figure 5). The straight-line plot obtained in figure 5 passes close to the origin, indicating that the catalyst is required for the photocatalysis of 4-Np. A plot of log (peak height) vs. log ZnPc loading results in a linear relationship, with a slope close to one, indicating that the degradation of 4-Np is first-order with respect to ZnPc (figure 6) [28].

3.3. *Comparative degradation of 4-Np*

The degree to which each phthalocyanine complex photocatalyses 4-Np was determined by comparing the HPLC trace obtained for $1 \times 10^{-5}\,\text{mol dm}^{-3}$ 4-Np solution before and after photolysis in the presence of individual photocatalysts in the visible region for 100 min. The results obtained for the percentage degradation of 4-Np are shown in figure 7. The trend in the photodegradation of 4-Np by the selected phthalocyanine complexes is as follows: ClAlPc $(89 \pm 8\%) >$ $ZnPcF_{16}$ $(75 \pm 5\%) >$ $ZnPc(NH_2)_4$ $(54 \pm 2\%) >$ ZnPc $(53 \pm 6\%) >$ $ZnPc(NO_2)_4$ $(45 \pm 3\%) >$ MgPc $(25 \pm 4\%) >$ $ZnPcCl_{16}$ $(23 \pm 1\%)$.

The use of ClAlPc as a heterogeneous photocatalyst resulted in the highest percentage degradation of 4-Np due to a number of characteristics of ClAlPc that contribute to its effectiveness as a photocatalyst. ClAlPc is monomeric in DMSO (figure 2), which reduces the quenching of the triplet state, leading to efficient transfer of energy from triplet state MPc to triplet oxygen [8]. Table 1 shows the triplet lifetimes and singlet oxygen quantum yields of MPcs in organic solvents. The data in table 1 give an indication of the relative triplet lifetimes and singlet oxygen quantum yields of the complexes, which will influence their photocatalytic activity. The rate of transfer of energy from the MPc triplet state to triplet oxygen is substantially reduced in water, as energy is dissipated as heat [29]. Aluminium is diamagnetic and therefore contributes to rapid intersystem crossing of the MPc complex [8, 26, 30, 31], leading to relatively high triplet (hence singlet oxygen)

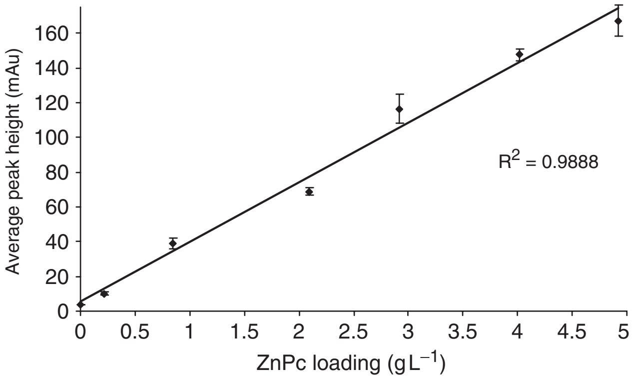

Figure 5. Plot of relative peak height *vs.* ZnPc loading to determine the effect of ZnPc on the phototransformation of 4-Np to fumaric acid ([4-Np] $= 1 \times 10^{-5}$ mol dm^{-3}, pH = 9).

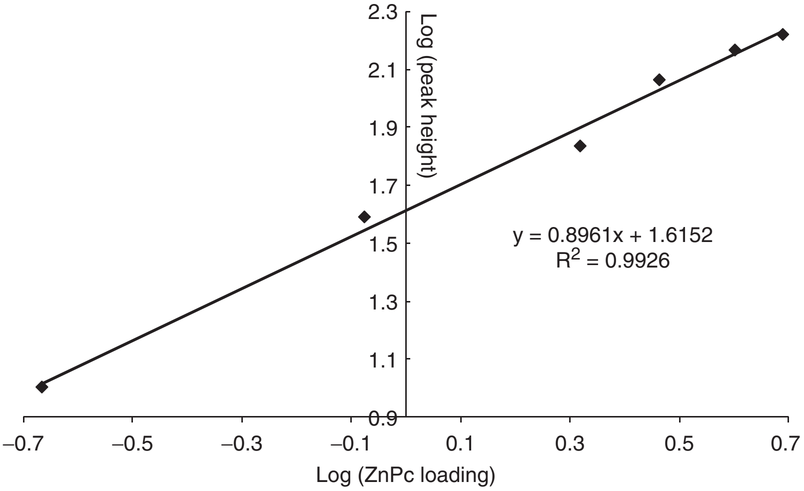

Figure 6. Plot of log (peak height) *vs.* log ZnPc loading to determine the reaction order with respect to ZnPc.

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quantum yields. The axial chlorine substituent also contributes to intersystem crossing by enhancing spin-orbit coupling due to the "heavy-atom" effect [32, 33] in ClAlPc. However, based on singlet oxygen quantum yields, ZnPc would be expected to perform better as a photocatalyst since it has a larger $\mathbf{\Phi}_{\Delta}$ value than ClAlPc in the same solvent. Table 1 shows that ClAlPc has the longest lifetime which could contribute to its effectiveness as a catalyst. The number of diffusional encounters between the triplet states of the MPc and ground state molecular oxygen increases with triplet state lifetime.

Aggregation in MPc complexes in solution is usually depicted as a coplanar association of rings progressing from monomer to dimer and higher-order complexes. In the complexes reported in this work, the MPc catalysts are not water soluble and are suspended as powder in aqueous solution. It is thus expected that the photocatalytic activity occurs on the surface of the particles. Since the

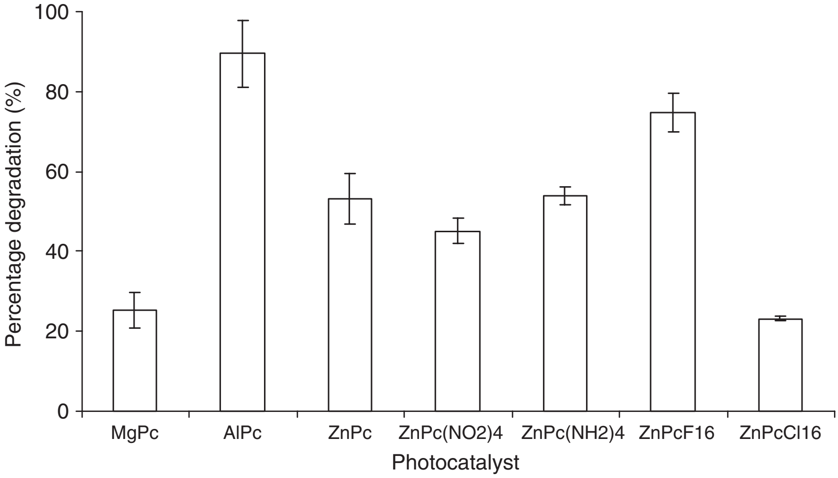

Figure 7. Percentage degradation of 4-Np by selected phthalocyanine complexes ([4-Np] = 1×10^{-5} mol dm^{-3}, pH = 9, irradiation time = 100 min).

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powder is suspended, the surface is not expected to show the aggregation behavior typical of MPcs in solution.

The degree of degradation of 4-Np obtained for $ZnPcF_{16}$ is relatively high compared to the other complexes in figure 7. Therefore, the high degree of degradation of 4-Np using $ZnPcF_{16}$ can be attributed to its triplet lifetime and to its high stability due to the presence of electron-withdrawing substituents [34]. $ZnPcCl_{16}$ would also be stable, but has an insignificant triplet lifetime, hence is less effective than $ZnPcF_{16}$. The ability of $ZnPc(NH_2)_4$ to degrade 4-Np to a large extent is unexpected, as amino groups are known to quench singlet oxygen [27]. However, figure 7 shows substantial photodegradation ability with $ZnPc(NH_2)$, comparable to ZnPc. This suggests that singlet oxygen mechanism (Type II) may not be the only mechanism involved in the photocatalyzed transformation of 4-NP in the presence of MPc complexes under discussion and under heterogeneous conditions. It is thus possible that Type I mechanism is also involved. In order to check the degree to which singlet oxygen is involved in the degradation of 4-Np, photocatalytic degradation of 4-Np in the presence of a singlet oxygen scavenger, DABCO, was carried out (using $ZnPc(NH_2)_4$ as an example). A comparison of the degradation of 4-Np in the presence and absence of DABCO is illustrated in figure 8. It is evident from figure 8 that the Type II mechanism is not the only means of 4-Np degradation, since there is still considerable degradation of 4-NP in the presence of DABCO.

3.4. *Mechanism for the photodegradation of 4-Np*

In order to confirm singlet oxygen involvement, the singlet oxygen scavenger, ADMA, was monitored spectroscopically to confirm formation of singlet state oxygen ($^1O_2$,$^1\Delta_g$) on irradiation of the suspended solid MPc with visible light [12, 35]. Figure 9 shows spectral changes that occur on exposure of ADMA to visible light in the presence of ClAlPc. The absorbance of ClAlPc is not observed as the MPc complex is not soluble.

The change in absorbance of ADMA shows that singlet oxygen is formed on photolysis of solid MPc in the presence of ADMA. The formed singlet oxygen will then be involved in the degradation of 4-Np. As mentioned above, radical ions (Type I mechanism) are also involved in the degradation of 4-Np (figure 8).

The final degradation products include fumaric acid and 4-nitrocatechol with reaction intermediates benzoquinone and hydroquinone. Fumaric acid as the final degradation product for 4-Np is important since the toxicity of fumaric acid is considerably lower than 4-Np: the ORAL-RAT LD_{50} value for 4-Np is $202\,mg\,kg^{-1}$, while that for fumaric acid is $9\,300\,mg\,kg^{-1}$ [36].

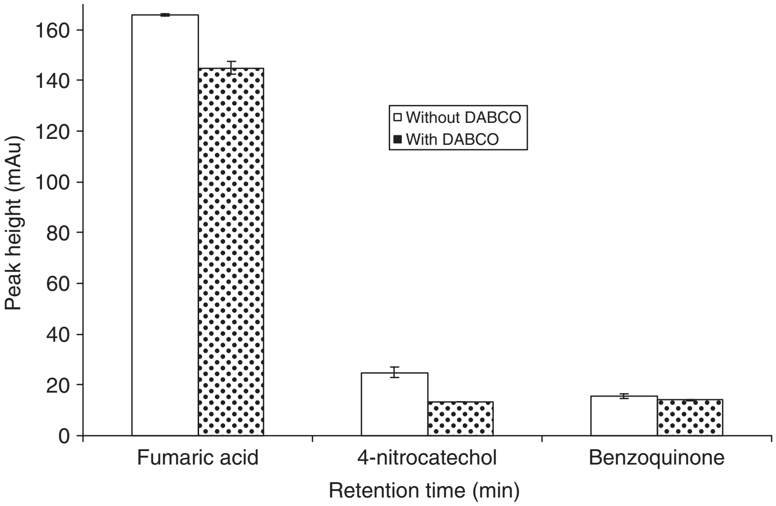

Figure 8. Comparison of the degree of formation of degradation products in presence and absence of a singlet oxygen scavenger (DABCO); ($[4\text{-Np}] = 1.0 \times 10^{-5}\,mol\,dm^{-3}$; pH = 9; irradiation time = 100 min).

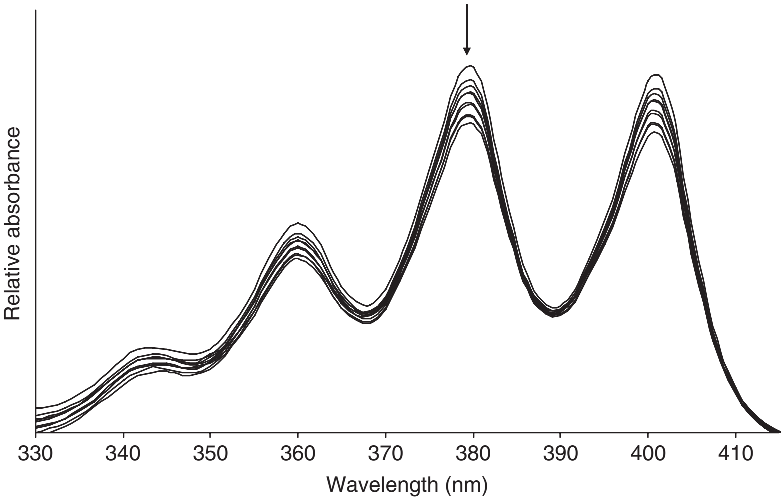

Figure 9. Electronic absorption spectral changes of ADMA during visible light photocatalysis in the presence of ClAlPc (ADMA concentration $= 6.9 \times 10^{-5}\,mol\,dm^{-3}$).

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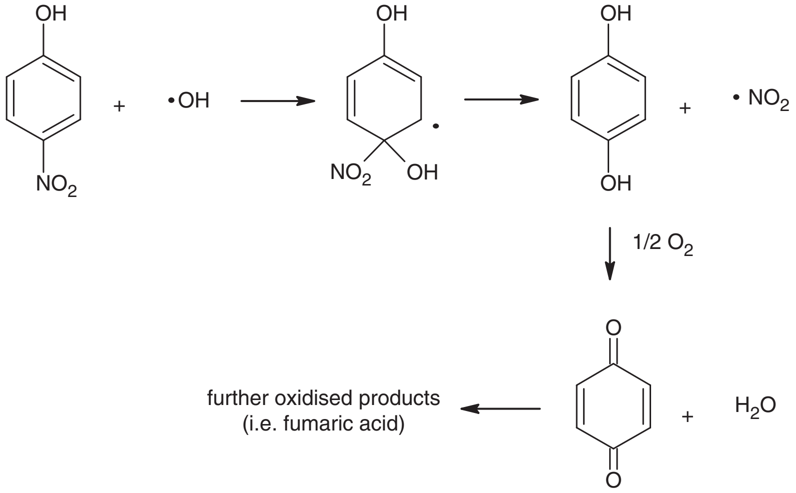
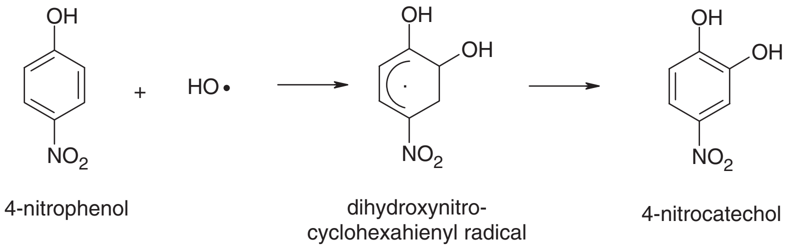
The proposed mechanism for the degradation of 4-Np to form fumaric acid follows a number of steps. The first step is the interaction of 4-Np with a hydroxyl radical generated from the Type I mechanism to form hydroquinone, followed by the oxidation of hydroquinone to form benzoquinone. Further oxidation of benzoquinone leads to the formation of fumaric acid (scheme 3). The hydroxyl radical in this reaction mechanism is the reaction initiator. The formation of 4-nitrocatechol occurs due to the addition of a hydroxyl radical ortho to the phenol functional group (scheme 4) [9]. The formation of 4-nitocatechol will similarly proceed according to scheme 4.

The proposed mechanism for the photodegradation of 4-Np in the presence of ZnPc photosensitizers under Type II mechanism may be represented as follows (scheme 5):



Scheme 3. Proposed mechanism for the transformation of 4-Np to benzoquinone in the presence of an MPc photocatalyst.



Scheme 4. Proposed mechanism for the transformation of 4-Np to 4-nitrocatechol in the presence of an MPc photocatalyst.

$$\mathrm{MPc} \xrightarrow{h\nu} {}^{1\mathrm{M}}\mathrm{Pc}^{*} \xrightarrow{\mathrm{isc}} {}^{3\mathrm{M}}\mathrm{Pc}^{*} \qquad (10)$$

$$^{3}\mathrm{O}_2 + {}^{3}\mathrm{MPc}^{*} \longrightarrow \mathrm{MPc} + {}^{1}\mathrm{O}_2 \qquad (11)$$

$$^{1}\mathrm{O}_2 + \text{4-Np} \longrightarrow \text{Products} \qquad (12)$$

Scheme 5. Transformation of 4-Np by singlet oxygen mechanism.

4. Conclusion

The MPc complexes: MgPc, ClAlPc, ZnPc, $ZnPc(NO_2)_4$, $ZnPc(NH_2)_4$, $ZnPcF_{16}$ and $ZnPcCl_{16}$, were employed as heterogeneous catalysts (suspended in aqueous solution of 4-Np) for the phototransformation of 4-Np. ClAlPc is the most successful catalyst, where $89 \pm 8\%$ degradation of 4-Np was achieved after 100 min. The lowest percentage degradations were obtained for $ZnPcCl_{16}$ and MgPc. The low degradation yields are due to short triplet lifetimes for both complexes and aggregation in the case of $ZnPcCl_{16}$. The major products formed due to the photodegradation of 4-Np include fumaric acid and 4-nitrocatechol. Reaction intermediates detected include hydroquinone and 1,4-benzoquinone.

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