

Comparative efficiency of immobilized non-transition metal phthalocyanine photosensitizers for the visible light transformation of chlorophenols

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Received 18 October 2005; received in revised form 8 December 2005; accepted 12 December 2005

Available online 23 January 2006

Abstract

Photolysis of aqueous solutions of chlorophenols (4-chlorophenol, 2,4-dichlorophenol, 2,4,5-trichlorophenol and pentachlorophenol) in the presence of immobilized non-transition metal phthalocyanine photosensitizers onto Amberlite® is presented. The photosensitizers studied are: Al (AlOCPc) and Zn (ZnOCPc) octacarboxyphthalocyanines; Al (AlPcS₄) and Zn (ZnPcS₄) tetrasulfophthalocyanines; sulfonated phthalocyanine complexes (containing mixtures of differently substituted derivatives) of Al (AlPcS_{mix}), Zn (ZnPcS_{mix}), Ge (GePcS_{mix}), Si (SiPcS_{mix}) and Sn (SnPcS_{mix}). Photolysis of the chlorophenols resulted mainly in the formation of chlorobenzoquinone derivatives. The complexes showed order of activity towards the transformation of pentachlorophenol as follows: ZnOCPc > SiPcS_{mix} > SnPcS_{mix} > ZnPcS_{mix} > GePcS_{mix} > ZnPcS₄ > AlPcS_{mix} > AlOCPc > AlPcS₄. The generation of singlet oxygen (¹O₂) by these immobilized MPC photosensitizers was found to play a major role in their photoactivities towards the transformation of these chlorophenols. Langmuir–Hinshelwood (L–H) kinetic model studies showed that the ZnOCPc, GePcS_{mix} and ZnPcS_{mix} photocatalysis occurred on the catalysts surface.

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Keywords: Aluminium; Zinc; Tin; Silicon; Germanium phthalocyanine; Pentachlorophenol; Amberlite® IRA-900; Photocatalyst

1. Introduction

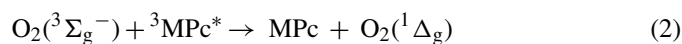
Phenols and the chlorinated phenols such as the 4-chlorophenol (4-CP), dichlorophenol (DCP), trichlorophenol (TCP) and pentachlorophenol (PCP) have long been recognized as extremely toxic environmental pollutants. The need for a facile transformation or degradation of phenols and chlorinated phenols to less harmful products has been of great research interest [1–12]. Hitchman et al. [1] have elegantly reviewed the various methods for the degradation of chlorophenols, which range from biological to chemical and to photochemical processes. UV irradiation represents an important means of degradation of chlorophenols [3]. Regrettably, however, direct irradiation of chlorophenols in water generates more toxic organic compounds (like the polychlorinated dibenzo-*p*-dioxins) than the parent compound. Also, the semiconductor, TiO₂ (band gap of 3.2 eV), widely used as a photocatalyst for the mineralization of chlorophenols absorbs in the UV region where only approximately 4% of solar radiation is effective [4]. To over-

come the above disadvantages, photosensitizers, which strongly absorb in the visible region are preferred. Metallophthalocyanine (MPC) photosensitizers are more efficient in photocatalytic reactions and also lead to the production of less harmful photoproducts [4–7,10–12]. Non-transition metallophthalocyanine complexes, such as Zn(II), Al(III) and Si(IV), exhibit excellent photosensitizing properties towards many environmentally relevant photo-assisted reactions.

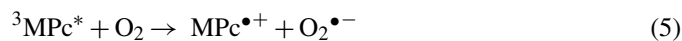
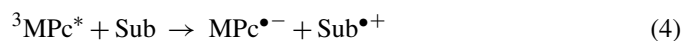
Photosensitized transformation of organic substrates or pollutants in aqueous media with MPC sensitizers mostly occur by the well-known type II mechanism (Eqs. (1)–(3)), which involves the generation of the highly oxidative singlet oxygen species responsible for the destruction of organic pollutants. The energy transfer starts with the excitation of the sensitizer by irradiation with visible light, which yields the excited singlet state (¹MPC^{*}) and then by intersystem crossing (isc), gives the excited triplet state (³MPC^{*}). This is followed by energy transfer from ³MPC^{*} to ground state (triplet) oxygen (³O₂, ³Σ_g⁻) that results in the generation of singlet oxygen (¹O₂, ¹Δ_g) followed by the oxidation of the substrate (sub):



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Type I mechanism (Eqs. (4)–(6)), which involves the participation of superoxide radical, may also take part in the reaction but this is generally limited:



An essential factor for these energy or electron transfer processes is the monomeric distribution of the photosensitizers. Aggregated and dimeric MPc sensitizers neither fluoresce nor show photochemical activity in energy transfer reactions probably due to enhanced radiationless excited state dissipation [13] and, therefore, reduction in the quantum yields of the singlet oxygen generation.

Oxidative transformation of polychlorophenols by phthalocyanine complexes electrostatically bound onto ion exchange resin (resulting in monomeric Pcs) show excellent catalytic activity and high stability [10]. In this work we report on the photocatalytic abilities of the following MPc photosensitizers (Fig. 1): Al (AlOCPc) and Zn (ZnOCPc) octacarboxyphthalocyanines; Al (AlPcS₄) and Zn (ZnPcS₄) tetrasulfophthalocyanines; sulfonated phthalocyanine complexes (containing mixtures of differently substituted derivatives) of Al (AlPcS_{mix}), Zn (ZnPcS_{mix}), Ge (GePcS_{mix}), Si (SiPcS_{mix}) and Sn (SnPcS_{mix}) towards the phototransformation of chlorophenols. Prior to this work, these types of photosensitizers have not been immobilized onto support such as Amberlite[®] nor investigated for the phototransformation of organic pollutants such as the chlorophenols. We chose these MPc photosensitizers because of their different photochemistry and photophysics characteristics and hence possible different photoactivity towards the degradation of pollutants. For example, AlPcS_{mix} and ZnPcS_{mix} complexes exhibit more monomeric behavior than their tetrasulfonated (AlPcS₄ and ZnPcS₄) counterparts in aqueous [11,12,14] and

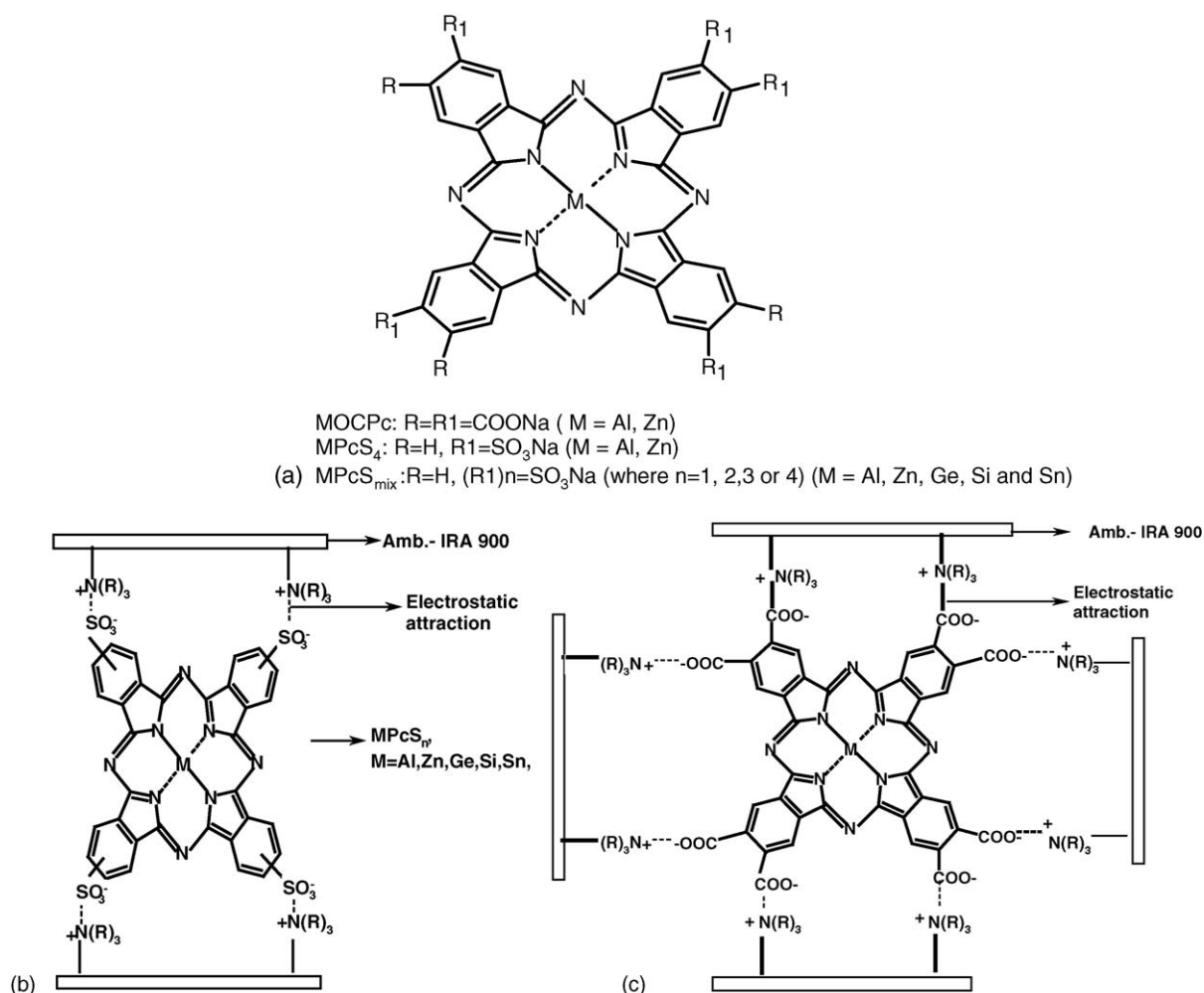


Fig. 1. (a) Molecular structure of the photosensitizers, (b) schematic representation of the tetrasulfonated MPc photosensitizers immobilized on Amberlite[®] and (c) schematic representation of the MOCPc photosensitizers immobilized on Amberlite[®].

non-aqueous [15] solutions and, hence better photoactivities towards photodegradation of chlorophenols in water. Tetrasulfometallophthalocyanine (MPcS₄) complexes such as those of the aluminium (AlPcS₄) [16] and zinc (ZnPcS₄) [17,18] aggregate in basic aqueous solutions in contrast to the corresponding octacarboxy complexes (AlOCPc and ZnOCPc) which exhibit monomeric behavior.

2. Experimental

2.1. Materials and reagents

AlPcS₄, ZnPcS₄ were synthesized, purified and characterized according to Weber and Busch method [19]. AlPcS_{mix}, ZnPcS_{mix}, GePcS_{mix}, SiPcS_{mix}, and SnPcS_{mix} complexes were synthesized from (Cl)AlPc, ZnPc, (OH)₂GePc, (OH)₂SiPc and (OH)₂SnPc, respectively, using fuming sulfuric acid (30% SO₃) according to literature procedure described for the AlPcS_{mix} [20]. AlOCPc and ZnOCPc were prepared, purified and characterized according to the reported procedure [21,22]. Amberlite[®] IRA-900 ion exchange resin was purchased from Aldrich and used as received. Phenol (SAARChem), 4-chlorophenol (Aldrich), 2,4-dichlorophenol (Aldrich), 2,4,5-trichlorophenol (Aldrich), pentachlorophenol, fumaric acid (SAARChem), 1,4-benzoquinone, 2-chloro-1,4-benzoquinone (Aldrich), 2,5-dichloro-1,4-benzoquinone (Aldrich), 2,3,4,5-tetrachloro-1,4-benzoquinone (Aldrich), hydroquinone (May and Baker) were of reagent grade, and were employed as either substrates or standards for high-pressure liquid chromatography (HPLC). Triply distilled deionized water was used for all the experiments. pH 10 boric acid buffer was employed for the photocatalytic studies, and pH 8 boric buffer was used for immobilization of MOCPc. Sodium azide was used as received from Sigma. Tetrasodium α,α -(anthracene-9,10-diyl) dimethylmalonate (ADMA) was a gift from Dr. V. Negrimovsky (from Organic Intermediates and Dyes Institute, Russia). All experiments were performed at $25 \pm 1^\circ\text{C}$.

2.2. Equipment and procedures

2.2.1. Immobilization of photosensitizers

The various MPc photosensitizer-Amberlite (represented as MPc-Amberlite) ion exchange resin compositions were prepared using the established procedure [23]. Unbuffered water was employed to deposit sulfonated MPc complexes onto Amberlite[®] supports. In order to ensure ionization of the MOCPc complexes, pH 8 boric acid buffer was employed for immobilization of these complexes onto Amberlite[®] instead of unbuffered water. The resin was thoroughly washed with water and dried. A 0.01 g of the resin was suspended in 100 ml solution of MPc with an absorbance of approximately 1. The reaction mixtures were left under gentle stirring with a magnetic stirrer and were monitored with Cary 500 UV-VIS-NIR spectrophotometer. For consistency, the immobilization was carried out until the number of moles of MPc immobilized was 5×10^{-8} mol. The change in absorbance values of the various aqueous MPc solutions was used to calculate the num-

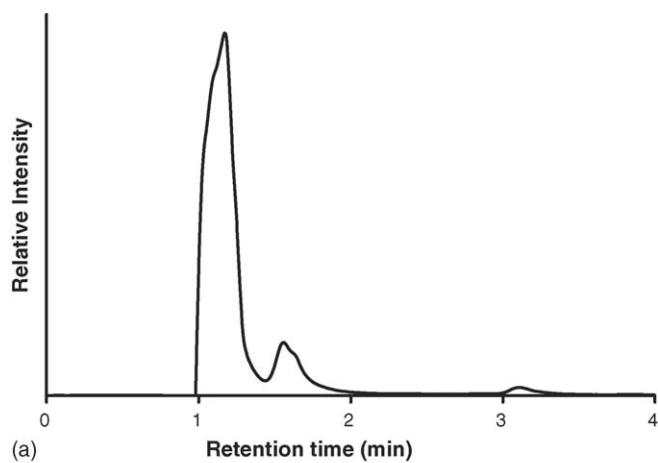
ber of moles of the MPc photosensitizer. In all cases 0.01 g of Amberlite[®] was employed for the immobilization, giving mol MPc/g Amberlite[®] loadings. In cases where we show the effects of aggregation (hence require large amounts of immobilized MPc), g MPc/g Amberlite[®] loading was employed and moles of MPc were not calculated due to aggregation at these high concentrations. Following immobilization, the coloured (light green or light blue) immobilized product obtained was first thoroughly washed with copious amount of distilled deionized water, then methanol and acetone, and finally dried in the oven at 70°C for 24 h. For recycling of immobilized MPc complexes, the used product was first washed with 0.01 mM H₂O₂ to remove the adsorbed chlorinated phenols and their oxidation products by oxidizing them. This was then followed by washing with water and ethanol, and then finally drying of the recycled product. Diffused reflectance spectra of the solid MPc-resin were recorded with Cary 500 UV-VIS-NIR spectrophotometer.

2.2.2. Photochemical studies

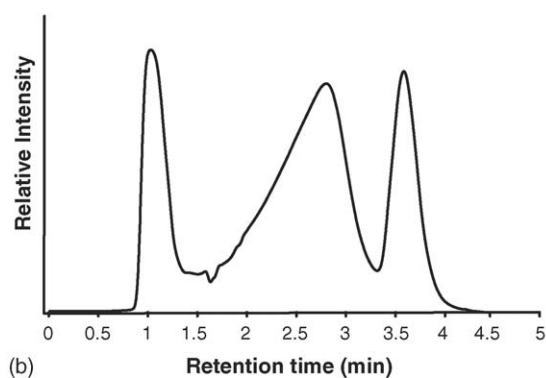
All photochemical studies were performed with a home-made photochemical set-up as described before [11,12]. Photolysis was performed in the visible region to avoid the effects of uncatalyzed photodegradation of the phenols in the ultra violet region. A 1 cm pathlength UV-vis spectrophotometer quartz cell fitted with a tight-fitting stopper was employed for the photocatalytic studies. Briefly, the set-up comprised of a light source from a General Electric Quartz lamp (300 W); using a 600 nm glass (Schott) and water filters to filter off UV and far infrared radiations, respectively. An interference filter (Intor, 700 nm with a bandwidth of 40 nm) was placed in the light path before the quartz cell containing the sample.

Typically, for the phototransformation of the chlorophenols, a 5 ml solution of the substrate containing 5×10^{-8} mol of immobilized photosensitizer on Amberlite[®] was first saturated with oxygen and then photolyzed under gentle stirring. The light intensity was measured with a power meter (Lasemate/A) and was found to be ca. 5×10^{16} photons $\text{s}^{-1} \text{cm}^{-2}$. Kinetic studies were monitored with UV-vis-NIR spectrophotometer or high pressure liquid chromatography (HPLC). Product identification (by spiking with standards and by comparing retention times) was carried out with the use of Quad-Gradient HPLC system, Agilent 1100 series fitted with an analytical column, μ -Bondapak-C18 (390 mm \times 3.00 mm) and connected to a variable wavelength UV-vis detector (set at $\lambda = 280$ nm). The mobile phase was made up of 70:30 methanol:water mixture. The volume of injected samples was 20 μl , and the elution rate was 1 ml/min.

Investigation of the singlet oxygen generation efficiencies of the immobilized photosensitizers was followed by photolysis of an aqueous (unbuffered) solution containing ADMA as chemical scavenger for singlet oxygen [24]. The participation of ¹O₂ in the photolysis was further confirmed by the addition of sodium azide (which is a ¹O₂ quencher) to the photolysis reaction containing the chlorinated phenols and the MPc photosensitizer.



(a)



(b)

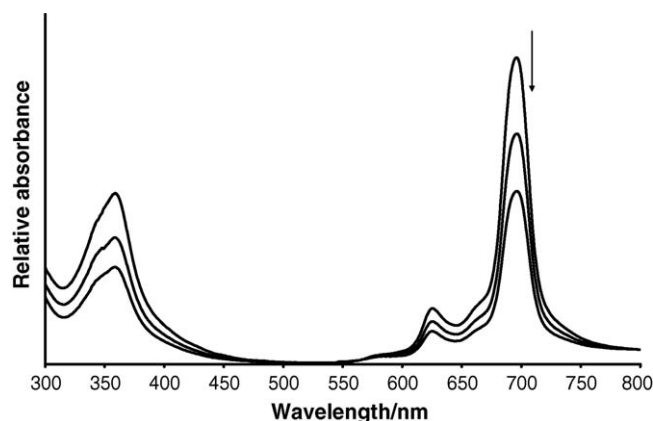
Fig. 2. (a) HPLC trace for GePcS_{mix}, (b) HPLC trace for ZnPcS_{mix}.

3. Result and discussion

3.1. Characterization of MPc complexes: immobilized or in solution

The nine MPc photosensitizers used in this study were synthesized and characterized as before [11,12]. Their spectroscopic characterization was consistent with literature. The extent of sulfonation for each of the five MPcS_{mix} (Fig. 1a, where M = Al, Ge, Si, Sn and Zn) complexes were obtained by HPLC (Fig. 2). It is expected that the most highly sulfonated (most soluble) would be the first to be eluted from the chromatographic column, and so give the lowest retention time and that the monosulfonated fractions give the highest retention times. The HPLC signals with the lowest retention times (~1 min) are assigned to the tetrasulfonated fractions, using tetrasulfozinc phthalocyanine (ZnPcS₄) as reference. AlPcS_{mix}, GePcS_{mix} and SiPcS_{mix} gave mainly the tetrasulfonated (Fig. 2a) and ZnPcS_{mix} and SnPcS_{mix} showed three main HPLC peaks confirming a large contribution of less sulfonated derivatives (Fig. 2b).

It is well known that the catalytic and photocatalytic activities of immobilized phthalocyanine complexes depend, amongst other factors, on the nature of the support [17,18]. Many literature reports on the immobilization of MPc complexes onto polymer supports involved interaction between the functionalized solid polymer and a suitably functionalized MPc leading to

Fig. 3. Electronic spectral changes with time of AIOCPc in aqueous (pH 8) solution during its immobilization on Amberlite[®] support. Starting concentration of AIOCPc = 1.42×10^{-5} M. Mass of Amberlite[®] = 0.01 g.

mainly covalently bonded MPc. In this work, Amberlite[®] IRA-900, was used. Amberlite[®] IRA-900 ion exchange resin is a strongly basic, macro-reticular resin of moderately high porosity with benzyltrialkylammonium functionality. Each of the sulfonated MPc sensitizers was attached to the resin by simply mixing it with resin beads in an aqueous solution (unbuffered). For the MOCPC complexes, pH 8 was employed in order to allow for ionization. Fig. 1b and c presents schematic representations of the immobilized sulfonated (Fig. 1b) and carboxylated (Fig. 1c) MPc complexes onto Amberlite[®]. The immobilization of the MPc onto the solid support was confirmed by the colour change of the polymer beads (white to light green or blue) and also by reflectance spectral measurements of the support following immobilization. It was observed that each MPc effectively bonded to the resin and, upon bonding, these MPc complexes cannot be easily removed by washing with solvents such as water, acetonitrile, and methanol. This was confirmed by the electronic spectral measurements of the ‘wash’ solvents, which did not show any detectable spectral bands (B or Q bands) characteristic of the MPc after soaking the MPc-resin in the respective solvents overnight.

The concentration of the MPc immobilized onto the solid support could be estimated spectroscopically by measuring the decrease in the absorbance of the Q band of the MPc after treating it with a known amount of the Amberlite[®]. Thus, this could conveniently be used to vary MPc loading per gram of Amberlite[®]. Fig. 3 is an example of spectral changes observed for the MPc sensitizer during immobilization of AIOCPc onto Amberlite[®]. Aggregation on MPc complexes is evidenced [25] by a high-energy band near 620 nm, and a low energy band near 670 nm (or higher) is due to the monomeric species. Fig. 4 shows diffuse reflectance UV–vis spectra of AlPcS₄ at different MPc loadings (g MPc/g Amberlite[®]), indicating that aggregation increases with increase in MPc concentration on the support as evident by the increase in the dimer peak at 645 nm. This behavior is due to self-association or intermolecular interactions between phthalocyanine complexes as the concentration of the immobilized MPc increases; the nature and processes that lead to this phenomenon are well described in the literature [18,26,27].

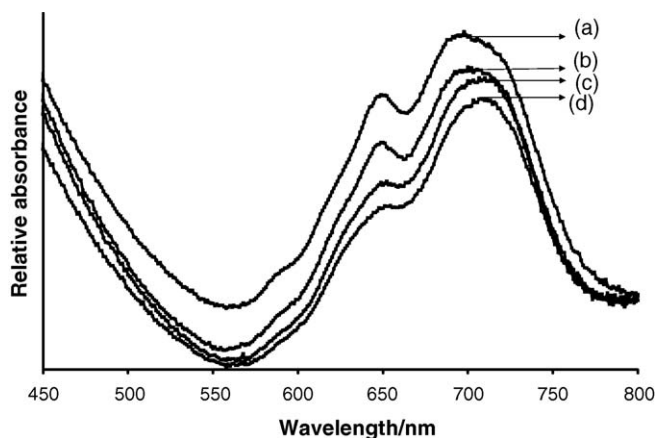


Fig. 4. Diffuse reflectance spectra of AlPcS₄-Amberlite showing the effects of aggregation. Different loading (%) on Amberlite® support (a) 1.25, (b) 1.00, (c) 0.75, (d) 0.5. Calculated from AlPcS₄ (g)/Amberlite® (g). The immobilization of AlPcS₄ on Amberlite® was carried out in unbuffered and allowed to proceed until the Q band of the photosensitizer disappeared completely.

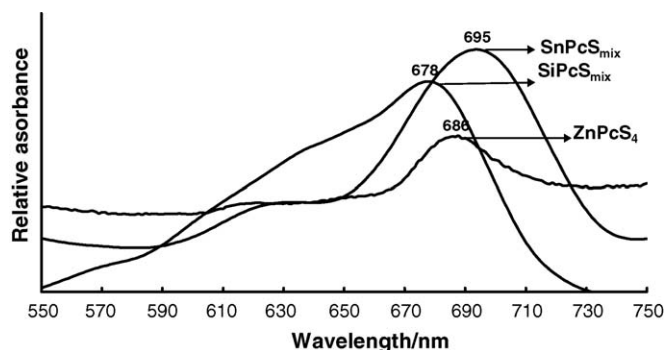


Fig. 5. Diffuse reflectance spectral ZnPcS₄-Amberlite, SnPcS_{mix}-Amberlite, and SiPcS_{mix}-Amberlite.

For studies shown in Fig. 4, moles of the MPc photosensitizer were not calculated due to aggregation of MPc at the high concentration employed (to show aggregation effects), hence the loadings are expressed as g MPc/g Amberlite®.

Fig. 5 compares the diffuse reflectance spectra of the immobilized MPc photosensitizers. As expected, mainly the low energy band due to the monomer is observed when the MPc com-

plexes were immobilized onto Amberlite®. A significant effect of immobilized MPc complexes (compared to solution spectra) was the shift in the Q band due to the monomeric species to lower energies (except for SiPcS_{mix}, AlPcS_{mix} and SnPcS_{mix}) (Table 1). Such a red shift is an indication that the energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the phthalocyanine is narrower than when it is in solution. The strong phthalocyanine–polymer interaction is expected to push the HOMOs of the phthalocyanine energetically up (decreasing the HOMO–LUMO gap) due to enhanced electron density on the π -framework caused by the tilted anionic sulfonato or carboxylic groups. Thus, the electronic transition from the low-lying filled π orbital to the π^* orbital (LUMO) would occur at lower energy. Inbaraj et al. [28] reported similar observation for tetrasulfometalloporphyrin complexes immobilized onto solid polystyrene support, which also was attributed to the distortion of the porphyrins from planarity.

3.2. Efficiency of singlet oxygen generation

All photochemical studies were restricted to the concentration 5×10^{-8} mol photosensitizer/Amberlite® (0.01 g) so that the photosensitization of the various MPcs could be compared.

The potential applications of these immobilized photosensitizers for water treatment will depend on the production rate of singlet oxygen in the aqueous system. The relative efficiencies of the generation of singlet oxygen by these sensitizers was monitored spectrophotometrically by following the decay of ADMA (a singlet oxygen scavenger) at $\lambda = 379$ nm. The rate of bleaching of ADMA is directly proportional to the production rate of singlet oxygen. Fig. 6 shows typical spectral changes observed for the degradation of ADMA during photosensitized reaction of the ZnOCPC supported onto Amberlite® in aqueous solution. In Fig. 6, the solution absorption spectrum of the MPc photosensitizer is not observed since MPc is immobilized on Amberlite®. Table 1 shows the percentage bleaching of ADMA by the photosensitizers, which is directly proportional to singlet oxygen production by the immobilized phthalocyanine complexes. From Table 1, singlet oxygen generation by the pho-

Table 1
Spectral, singlet oxygen generation and chlorophenol percentage conversion data obtained for the MPc complexes

Catalyst	ϵ ($\times 10^5$)	Q band in aqueous solution ^a	Q band on support ^b	% degradation of 7.4×10^{-5} M ADMA	% conversion of 1×10^{-3} M PCP
AlOCPc	0.79	696	708	7.5	10.7
AlPcS ₄	1.58	678	710	3.8	6.2
AlPcS _{mix}	1.51	674	675	18.9	10.7
ZnOCPC	1.82	688	698	41.5	29.8
ZnPcS ₄	0.35	636(d), 680(m)	686	20.8	12.8
ZnPcS _{mix}	0.78	672	679	26.4	21.1
GePcS _{mix}	1.02	675	685	30.2	16.5
SnPcS _{mix}	1.30	645(d), 698(m)	695	30.2	24.4
SiPcS _{mix}	1.74	680	678	43.7	26.0

^a Electronic absorption spectra, d = dimer; m = monomer.

^b Diffuse reflectance spectra.

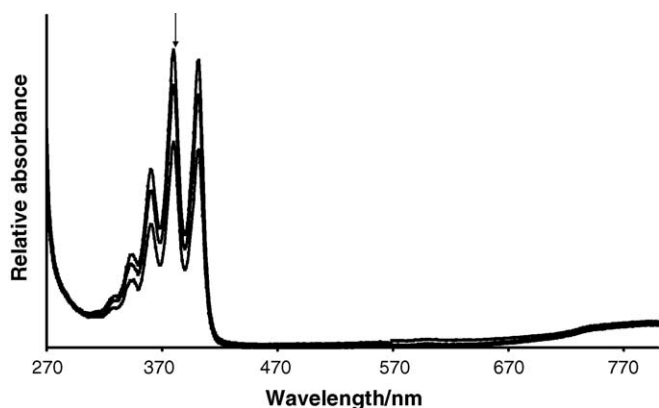


Fig. 6. Electronic absorption spectral changes of ADMA during visible light photolysis, catalyzed by ZnOCPc-Amberlite. ADMA concentration = 7.4×10^{-5} M.

tosensitizers follows the following trend: $\text{SiPcS}_{\text{mix}} > \text{ZnOCPc} > \text{GePcS}_{\text{mix}} = \text{SnPcS}_{\text{mix}} > \text{ZnPcS}_{\text{mix}} > \text{ZnPcS}_4 > \text{AlPcS}_{\text{mix}} > \text{AlOCPc} > \text{AlPcS}_4$. In DMF, where aggregation is expected to be minimal, Gerdes et al. [6] reported the following trend: $\text{ZnPcS}_4 > \text{SiPcS}_4 > \text{GePcS}_4 > \text{AlPcS}_4$, for singlet oxygen production which is comparable to the singlet oxygen generation reported in this work (considering the same ring system and changes in the central metal), except for ZnPcS_4 . The participation of $^1\text{O}_2$ in the photocatalysis was further confirmed by the addition of sodium azide, which is a $^1\text{O}_2$ quencher, to the chlorinated phenol photocatalysis reaction. Photocatalysis did not occur with any of the immobilized MPc in the presence of sodium azide, hence confirming the participation of the singlet oxygen in this photocatalytic reaction.

3.3. Photosensitized transformation of chlorophenols

3.3.1. Optimization of phototransformation conditions using PCP

It is important to note that in the absence of immobilized photosensitizer no transformation of the chlorophenols was observed following the photolysis in the Q band region of the MPc sensitizer. Also without photolysis, no transformation of the chlorophenols occurred in the presence of the photosensitizer. In order to determine the optimum amount of immobilized catalyst needed for the photosensitized transformation of the phenols, 2.5×10^{-3} M PCP (as an example) was photodegraded using different moles of the immobilized ZnOCPc (Fig. 7). It was found that phototransformation of PCP (for 5 min) showed increase in the rate (determined by change in absorbance) with increase in the moles of the ZnOCPc immobilized on Amberlite® until the mole ratio of ZnOCPc to PCP was 1:99. Further increase in the mole ratio did not result in the increase in the rate of phototransformation of PCP (Fig. 7), suggesting that the best mole ratio of the immobilized MPc to PCP for a successful photodegradation reaction is approximately 1:99. This behavior suggests excellent photocatalytic activity.

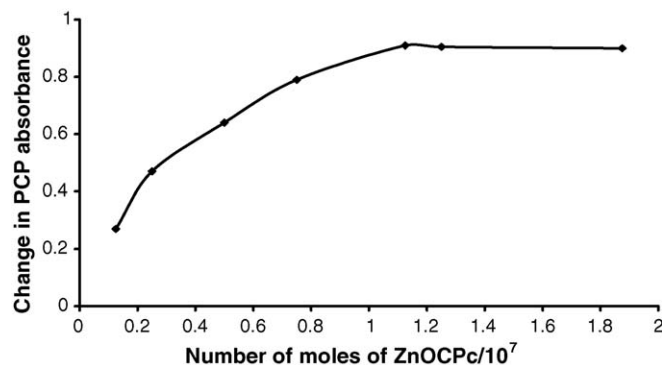


Fig. 7. Effects of changing the concentration of ZnOCPc immobilized on Amberlite® on the % conversion of 2.5×10^{-3} M, PCP solution, as judged by the decrease in the absorbance spectra of the latter. Photolysis time was 5 min.

3.3.2. Phototransformation of chlorophenols

UV–vis spectroscopy and HPLC were employed to monitor the transformation of chlorophenols. Fig. 8 shows spectral changes which are typical for photosensitized transformation of the chlorophenols (4-CP is used as an example in Fig. 8). The band at 280 nm is due to 4-CP band while the two at 240 and 300 nm are due to the product (benzoquinone). The identity of benzoquinone and 4-CP bands was confirmed by recording the spectra of each in the absence of the MPc. As with singlet oxygen experiment, ZnOCPc loading of 5×10^{-8} mol/g Amberlite® was maintained for the comparative study of the photosensitized transformation of the chlorophenols (10^{-3} M). The photosensitized transformation activity with these MPc complexes followed a trend (4-CP > DCP > TCP > PCP) (Fig. 9) similar to that reported for these sensitizers in aqueous solution [11,12], suggesting greater difficulty in photodegradation as the chlorine substituents increases. To compare the photosensitized effi-

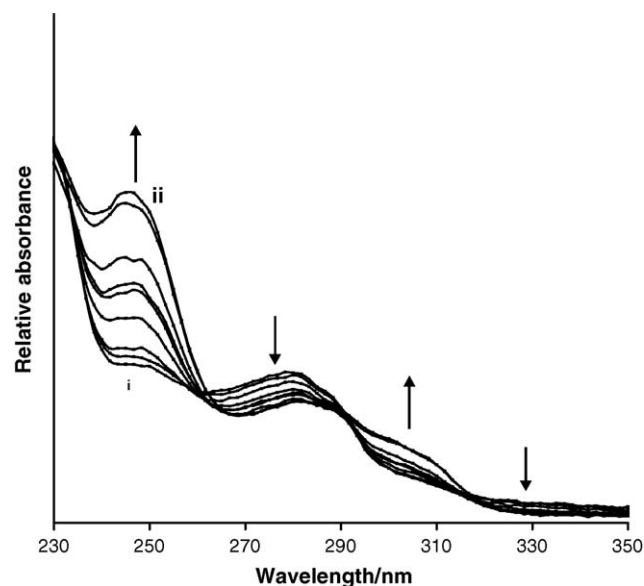


Fig. 8. Electronic absorption spectral changes of 1×10^{-3} M 4-CP during its visible light photocatalysis in the presence of ZnOCPc-Amberlite. The spectra were recorded 1 min intervals.

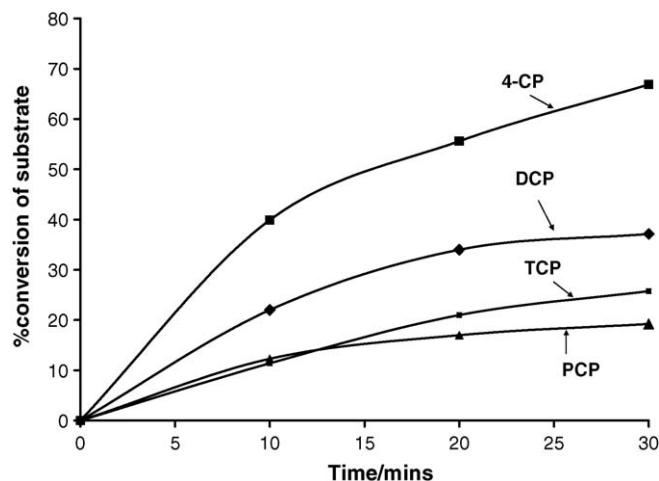


Fig. 9. Plots of % conversion (from HPLC traces) of chlorophenols vs. time for the photocatalysis of 1 mM of chlorophenols in the presence of AITSPc-Amberlite.

iciencies of the various immobilized MPc complexes, PCP was chosen as a substrate. The experiment was performed at the optimized immobilized MPc: PCP ratio (1:99, mol/mol) at pH 10 conditions. Table 1 compares the percentage conversion of PCP in the presence of the MPc sensitizers and shows that the order of photoactivity of the MPc complexes was as follows: ZnOCPc > SiPcS_{mix} > SnPcS_{mix} > ZnPcS_{mix} > GePcS_{mix} > ZnPcS₄ > AlPcS_{mix} > AlOCPc > AlPcS₄. One of the remarkable results in this work is the high efficiency of ZnOCPc over SiPcS_{mix} which is known for its high photocatalytic efficiency [29]. The rate of singlet oxygen generation affected the photocatalytic activity. Comparing trends of generation of singlet oxygen by the photocatalysis (Table 1) with the above trends for photodegradation of PCP, show similarities, except for GePcS_{mix} which shows a larger rate of singlet oxygen production than ZnPcS_{mix}, but shows a lower photocatalytic activity than the latter. Also SiPcS_{mix} shows a larger singlet oxygen production rate than ZnOCPc but less catalytic activity towards the transformation of chlorinated phenols.

Fig. 10 presents examples of HPLC chromatograms obtained on photocatalysis of the chlorophenols, using PCP and DCP as examples. The main products of the chlorophenol photooxidation were found to be the benzoquinone derivatives of the chlorophenols, confirmed by spiking with standard samples and by retention times. Thus, PCP gave 2,3,5,6-tetrachloro-1,4-benzoquinone (TCBQ), TCP gave 2,5-dichloro-1,4-benzoquinone (DCBQ), DCP gave 2-chloro-1,4-benzoquinone (CBQ) and 4-CP gave benzoquinone (BQ). Traces of fumaric acid (FA) were obtained for DCP (Fig. 10b). The photodegradation of the chlorophenols may be represented by the proposed mechanism as shown by Schemes 1a and b.

One of the most important factors in the large-scale application is the photostability of the photosensitizers is the ability to recycle the catalysts; three repetitive experiments were performed by re-using MPc immobilized on Amberlite®, for fresh PCP (2×10^{-3} M) solution each time, as shown in Fig. 11 using

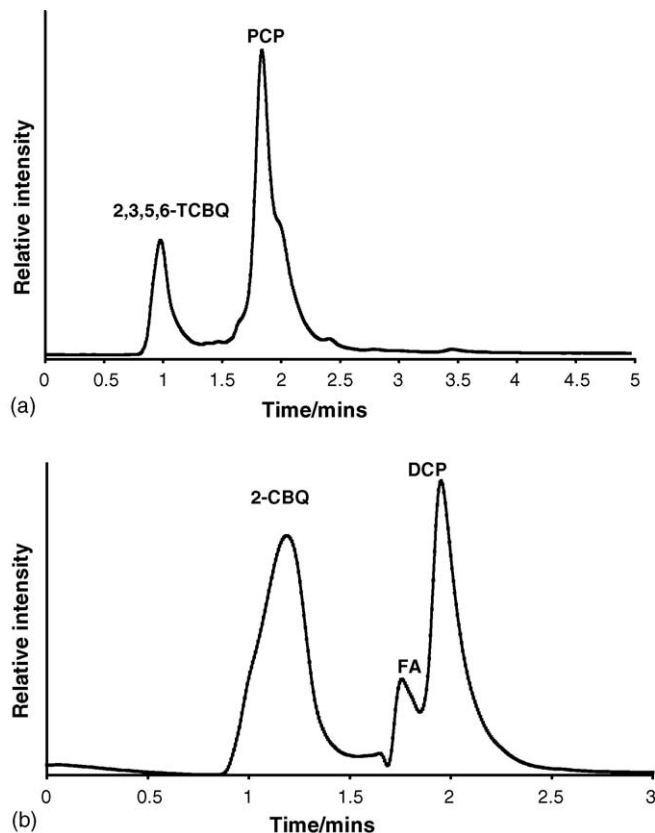
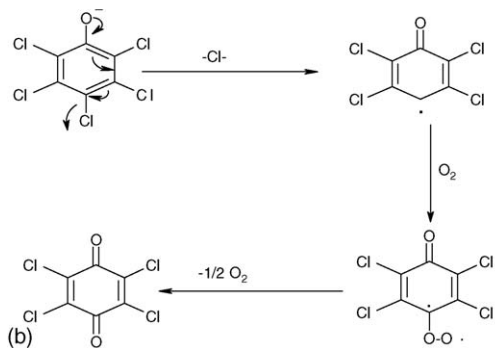
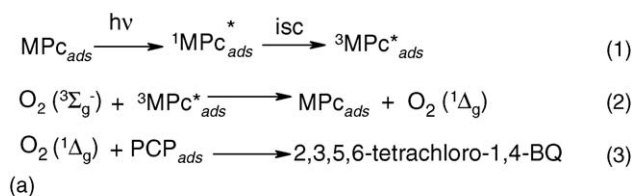


Fig. 10. (a) HPLC chromatogram of the reaction mixture after 1×10^{-3} M PCP photocatalysis (in the presence of ZnOCPc-Amberlite) showing formation of a new peak at $t = 1$ min identified as 2,3,5,6-benzoquinone and the PCP peak at $t = 1.8$ min. TCBQ = tetrachloro benzoquinone. (b) HPLC chromatogram of the reaction mixture after 10^{-3} M DCP photocatalysis (in the presence of ZnOCPc-Amberlite) showing formation of new peaks at $t = 1.2$ min identified as 2-chlorobenzoquinone and a peak at $t = 1.8$ min identified as fumaric acid. The DCP peak is at 1.9 min. CBQ = chlorobenzoquinone, FA = fumaric acid.

ZnOCPc as an example. High stability of the catalyst is observed on re-using it. The immobilized ZnOCPc and all the other catalysts did not show any observable degradation after use, this was confirmed by the diffuse reflectance spectra.

Generally, we observed that all the immobilized MPc photosensitizers could be repeatedly used for the photosensitized transformation of the chlorophenols without significant loss of activity. Under homogeneous conditions, photodegradation of 4-CP using ZnOCPc, results in the rapid degradation of this sensitizer (>51% in 3 min) [11], thus making it most unsuitable for use for the photosensitized transformation of higher chlorinated phenols such as TCP and PCP. All the MPc complexes discussed in this work showed the similar stability on re-use as observed ZnOCPc (Fig. 11). Compared to homogeneous conditions, the catalysts reported in this work showed superior photocatalytic properties towards the degradation of chlorinated phenols when immobilized onto Amberlite®. The immobilized catalysts retained their activities even after 6 months on storage at ambient temperature, thus demonstrating an excellent long-term stability of these immobilized MPc complexes on the supports.



Scheme 1. (a) The mechanism of generation of singlet oxygen by an adsorbed (ads) MPC photosensitizer, followed by transformation of adsorbed (ads) pentachlorophenol to the benzoquinone derivative. Similar equations will apply to the other chlorophenols. ISC = intersystem crossing. MPC represents ZnOCPC, GePC_{mix} and ZnPC_{mix} where Langmuir–Hinshelwood model showed adsorption of PCP. (b) Proposed mechanism for the transformation of PCP to the benzoquinone derivative in the presence of singlet oxygen. Similar mechanism may be derived for the other chlorophenols.

3.4. Langmuir–Hinshelwood (L–H) kinetic model

The L–H model has widely been employed to treat the dependency of heterogeneous photocatalytic reaction rates on the concentrations of chlorinated aromatics and other organic substrates [30,31]. L–H model (Eq. (7)) describes the competitive adsorption of substrates, reaction intermediates and chlorophenol oxidant products, and assumes that all intermediate products have the same binding characteristics to the photosensitizers as the parent substrate [30,31]:

$$\frac{1}{\text{rate}} = \frac{1}{k_r} + \frac{1}{k_r K_{ad} C_{sub}^0} \quad (7)$$

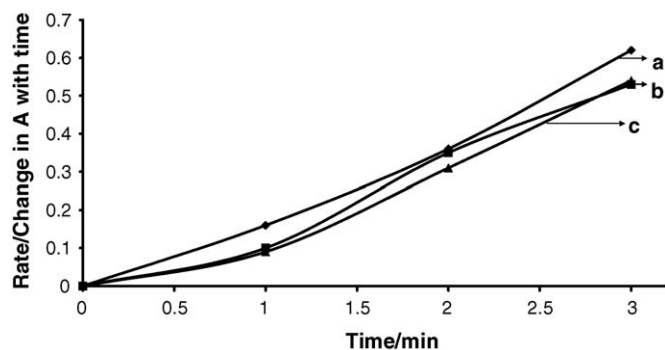


Fig. 11. Kinetic plots (change in absorbance against time) for the photocatalysis of three fresh solutions of 2×10^{-3} M PCP performed by re-using the same ZnOCPC-Amberlite catalyst for different PCP samples: (a) fresh ZnOCPC-Amberlite catalyst, (b) re-use of the catalyst in a fresh sample of PCP solution, (c) further re-use of the same catalyst in another fresh sample of PCP solution.

Table 2
The LHKM parameters details of the photocatalysis of PCP

Catalyst	R^2 value	k_r (min^{-1})	K_{ad} (mol^{-1} l)
AlPC _{S4}	0.8357	0.37	0.63
AlOCPC	0.8409	1.02	0.16
AlPC _{mix}	0.8912	0.45	1.21
ZnPC _{S4}	0.3815	0.37	4.87
GePC _{mix}	0.9842	0.63	1.72
ZnPC _{mix}	0.9945	0.96	1.11
SnPC _{mix}	0.8561	1.09	1.03
SiPC _{mix}	0.6507	1.04	1.34
ZnOCPC	0.9387	1.01	2.15

where k_r is the apparent reaction rate constant, K_{ad} the adsorption coefficient and C_{sub}^0 is the initial concentration of the substrate (in this case we used PCP as an example). The rate refers to the degradation of the chlorophenols as judged by the disappearance of the spectra of the substrates or the reduction in the intensity of the HPLC traces.

In this work, the change in PCP absorbance with time was used as an example. Table 2 shows the kinetic parameters obtained from the plots. Relatively high degree of linearity was obtained with $r^2 = 0.9387$, 0.9842 and 0.9945 for the ZnOCPC, GePC_{mix} and ZnPC_{mix}, respectively, indicating that the reactions occurred mainly on the surface of these photocatalysts. The relatively high K_{ad} values for ZnOCPC, ZnPC_{S4} and GePC_{mix}, imply sufficient adsorption of PCP onto the catalyst. The reason for the relatively low K values for the AlPC_{S4} and AlOCPC photocatalysis cannot be ascertained for now but low K_{ad} values are generally attributed to competition between the substrates and reaction intermediates.

4. Conclusions

We have shown in this work that various immobilized photosensitizers catalyzed visible light photolysis of chlorophenols. Singlet oxygen played a major role in the photolysis reactions. The L–H kinetic model also showed that for ZnOCPC, ZnPC_{mix} and GePC_{mix} photocatalysis, appreciable heterogeneous catalysis took place. It was observed that ZnOCPC which degrades rapidly in aqueous solutions is very stable when immobilized. The photoactivity of the MPC complexes towards transformation of chlorophenols was as follows: ZnOCPC > SiPC_{mix} > SnPC_{mix} > ZnPC_{mix} > GePC_{mix} > ZnPC_{S4} > AlPC_{mix} > AlOCPC > AlPC_{S4}. The results reported in this work provide a basis for development of MPC complexes for the transformation of chlorophenols in water.

Acknowledgements

We thank Rhodes University, the National Research Foundation (NRF, GUN 2053657 and GUN 2069275) and the Andrew Mellon Foundation for Accelerated Development Programme for their supports. B.A. is grateful to the ICSC World Laboratory for a PhD scholarship.

References

- [1] M.L. Hitchman, R.A. Spackman, N.C. Ross, C. Agra, *Chem. Soc. Rev.* 24 (1995) 423.
- [2] A.G. Agrios, K.A. Gray, E. Weitz, *Langmuir* 19 (2003) 1402.
- [3] S. Vollmuth, A. Zajc, R. Niessner, *Environ. Sci. Technol.* 28 (1994) 1145.
- [4] A.M. Volodin, *Catal. Today* 58 (2000) 103.
- [5] N. Nensala, T. Nyokong, *Polyhedron* 16 (1997) 2971.
- [6] R. Gerdes, D. Wöhrle, W. Spiller, G. Schneider, G. Schnurpfeil, G.J. Schulz-Ekloff, *J. Photochem. Photobiol. A: Chem.* 111 (1997) 65.
- [7] Y.I. Skurlatov, L.S. Ernestova, E.V. Vichutinskaya, D.P. Samsonov, I.V. Semenov, K.O. Rod, V.O. Shvidky, R.I. Pervunina, T.J. Kemp, *J. Photochem. Photobiol.* 107 (1997) 207.
- [8] M. Nowakowska, K. Szczubialka, *J. Photochem. Photobiol.* 91 (1995) 81.
- [9] M. Nowakowska, K. Szczubialka, S. Zapotoczny, *J. Photochem. Photobiol.* 97 (1996) 93.
- [10] T. Ichinohe, H. Miyasaka, A. Isoda, M. Kimura, K. Hanabusa, H. Shirai, *React. Funct. Polym.* 43 (2000) 63.
- [11] K. Ozoemena, N. Kuznetsova, T. Nyokong, *J. Photochem. Photobiol. A: Chem.* 139 (2001) 217.
- [12] K. Ozoemena, N. Kuznetsova, T. Nyokong, *J. Mol. Catal. A: Chem.* 176 (2001) 29.
- [13] A. Harriman, G. Poter, M.C. Richoux, *Coord. Chem. Rev.* 44 (1982) 83.
- [14] R. Edrei, V. Goofried, J.E. van Lier, S. Kimel, J. Porphyr. Phthalocyan. 2 (1998) 191.
- [15] A. Ogunsipe, J.-Y. Chen, T. Nyokong, *New J. Chem.* 28 (2004) 822.
- [16] J.L. Bourdelande, M. Karzazi, L.E. Dixelio, M.I. Litter, G.M. Tura, E. San Roman, V. Vinent, *J. Photochem. Photobiol. A: Chem.* 108 (1997) 273.
- [17] V. Iliev, A. Ileva, *J. Mol. Catal. A: Chem.* 103 (1995) 147.
- [18] V. Iliev, D. Tomova, *Catal. Commun.* 3 (2002) 287.
- [19] J.H. Weber, D.H. Busch, *Inorg. Chem.* 4 (1965) 469.
- [20] M. Ambroz, A. Beeby, A.J. MacRobert, M.S.C. Simpson, R.K. Svendsen, D. Phillips, *J. Photochem. Photobiol. B: Biol.* 9 (1991) 87.
- [21] N. Kuznetsova, N.S. Gretsova, O. Yuzhakova, V. Negrimovsky, O. Kaliya, *Zh. Obsch. Khim.* 71 (2001) 36.
- [22] K. Sakamoto, E. Ohno, *Prog. Org. Coat.* 31 (1997) 139.
- [23] A. Sorokin, B.J. Meunier, *J. Chem. Soc., Chem. Commun.* (1994) 1799.
- [24] N.A. Kuznetsova, N.S. Grtsova, V.M. Derkacheva, O.L. Kaliya, E.A. Lukyanets, *J. Porphyr. Phthalocyan.* 7 (2003) 147.
- [25] M.J. Stillman, T. Nyokong, in: C.C. Leznoff, A.B.P. Lever (Eds.), *Phthalocyanines: Properties and Applications*, vol. 1, VCH Publishers, New York, 1989.
- [26] G. Schneider, D. Wöhrle, W. Spiller, J. Stark, G. Schulz-Ekloff, *Photochem. Photobiol.* 60 (1994) 333.
- [27] T. Buck, H. Bohlen, D. Wöhrle, G. Schulz-Ekloff, A.J. Andreev, *Mol. Catal.* 80 (1993) 253.
- [28] I.J. Inbaraj, M.V. Vinodu, R.G. Gandhidasan, R. Murugesan, M. Padmanbhan, *J. Appl. Polym. Sci.* 89 (2003) 3925.
- [29] D. Wöhrle, O. Surorova, R. Gerdes, O. Bartels, L. Lapok, N. Baziakina, S. Makarov, A. Slodek, *J. Porphyr. Phthalocyan.* 8 (2004) 1020.
- [30] H. Al-Ekabi, N. Serpone, *J. Phys. Chem.* 92 (1988) 5726.
- [31] D.D. Dionysiou, A.P. Khodadoust, A.M. Kern, M.T. Suidan, I. Baudin, J.-M. Laine, *Appl. Catal. B: Environ.* 24 (2000) 139.