



Photooxidation of 4-chlorophenol sensitized by lutetium tetraphenoxy phthalocyanine anchored on electrospun polystyrene polymer fiber

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ABSTRACT

An electrospun polystyrene (PS) fiber incorporating tetraphenoxy phthalocyanine complex of lutetium (LuTPPc/PS) as a photosensitizer was applied for the degradation of 4-chlorophenol in aqueous solution in the presence of visible light. The photocatalytic activity of the LuTPPc in the fiber was compared to that of zinc phthalocyanine (ZnPc) incorporated into the PS fiber, and the former showed higher activity. UV–Vis spectral changes of sample solutions indicated transformation of the analyte with first order kinetics and half-lives that are within one and half hours for LuTPPc/PS. Products identified from the spectral changes and gas chromatography were benzoquinone, hydroquinone and 4,4'-dihydroxydiphenol suggesting that the photodegradation of 4-chlorophenol was through both Types I and II mechanisms.

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1. Introduction

Photocatalysis has been recognized as a promising technique for water and air purification and has since been studied extensively as an alternative to currently used technologies, such as chlorination, ozonation and adsorption on active carbon [1,2]. There have been reports of photocatalysis involving inorganic compounds that use the ultra violet (UV) part of the solar spectrum [3,4].

There has been a growing interest in the use of dyes such as phthalocyanines (Pcs) in photosensitized catalytic applications [5,6]. This is due to their excellent absorption of visible light [7], high stability and remarkable photoactivity [8]. Most importantly, the ability of some of these phthalocyanines to efficiently produce reactive singlet oxygen from ground state molecular oxygen in the presence of light is of much interest since singlet oxygen is a good candidate for oxidative processes [9]. However, most of the reported photosensitized reactions involving phthalocyanines usually occur in homogeneous media, thus rendering recycling of the phthalocyanine very difficult. There have been attempts to anchor these phthalocyanines onto insoluble support systems such as amberlite [10,11], silica and zeolite [6] as well as polycrystalline titanium oxide [12] for heterogeneous catalysis. Anchoring of phthalocyanines onto electro-spun nanofibers for use in photocatalysis has not been explored. These nanofabric materials have the advantage of large surface area that would enhance the catalytic activity of the phthalocyanine immobilized on them.

Functionalisation of nanofibers through the integration of functional molecules into solid polymer fiber core has been found to be desirable in many fields such as biosensor technology [13], tissue engineering [14], drug delivery [15] and nanoelectronics [16] due to the large surface area of these nanofibers. Incorporation of phthalocyanines into electro-spun polymer fibers has been reported with the functionality of the phthalocyanine maintained in the solid fiber core [17,18]. Mosinger et al., reported that a ZnPc anchored on polyurethane polymer fiber led to a red shifted Q-band compared to those recorded in some solvents [19]. Such a red shift is desirable and very promising in harvesting visible light for applications in photosensitized catalysis.

Chlorophenols are very common aqueous organic pollutants, partly because of their importance in the production of fungicides and herbicides. They are also present in effluents of pulp mills. As a result of the immense economic importance associated with the removal of chlorophenols during water purification, various attempts to oxidize these pollutants have been described [20,21].

There has been considerable investigation into the degradation of phenols using oxidants in the presence of catalysts such as metallophthalocyanines (MPcs). The use of oxidants in the degradation of chlorophenols (and related molecules) to less harmful products has proven to be successful [22–26]. However, processes involving no oxidants are still preferred to avoid the harmful effects of the toxic oxidants.

In this paper we demonstrate the photosensitized oxidation ability of a phthalocyanine anchored onto a polystyrene polymer fiber in the degradation of 4-chlorophenol as model organo-chlorinated pollutant. Tetraphenoxy-phthalocyanine complex of lutetium(III) (LuTPPc, Fig. 1) was anchored onto a polystyrene (PS) polymer fiber by electrospinning. The choice of lutetium was

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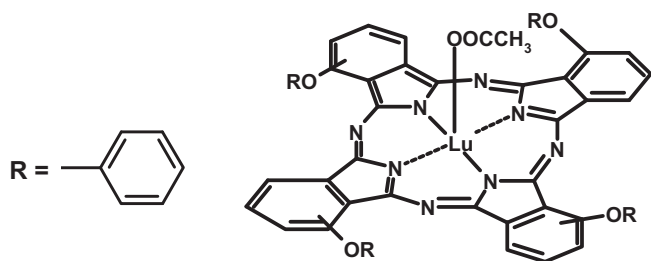


Fig. 1. Molecular structure of LuTPPc.

influenced by its larger size which will encourage intersystem crossing to the triplet state, hence generating singlet oxygen which is required for photocatalysis. Also the applications of the lanthanide phthalocyanines in photocatalysis are still rare in the literature. The bulky substituent was chosen to minimize aggregation which is a major problem with phthalocyanines. The photocatalytic activity of the LuTPPc/PS is compared with that of a simple MPc using zinc phthalocyanine (ZnPc/PS) as an example.

2. Experimental

2.1. Materials

Polystyrene (PS, Mw = 192,000 g/mol), *N,N*-dimethylformamide (DMF) and tetrahydrofuran (THF) were from MERCK Chemical Ltd, anthracene-9,10-bis-methylmalonate (ADMA), 1,4-benzoquinone 98%, zinc phthalocyanine (ZnPc) and sodium azide 99%, sodium hydroxide/di-sodium hydrogen phosphate were from Aldrich. 1-Pentanol was from SAARCHEM. 4-Chlorophenol 99% was from Fluka while hydroquinone was obtained from May and Baker LTD.

2.2. Synthesis

The synthesis of LuTPPc has been reported [27] and its molecular structure is shown in Fig. 1. The electrospinning technique with or without Pc complexes has been described [17,18,28]. For the current work, the LuTPPc/PS or ZnPc/PS electrospun fiber was formed as follows: a solution containing 2.5 g (1.3×10^{-5} moles of polystyrene and 1.35 mg (1.2×10^{-6} moles) of LuTPPc (or ZnPc) in 10 ml DMF/THF(4:1) was stirred for 24 h to produce a homogeneous solution. The solvent mixture was employed to allow both PS and LuTPPc (ZnPc) to dissolve. The solution was then placed in a cylindrical glass tube fitted with a capillary needle. A potential difference of 20 kV (–5 to 15 kV) was applied to provide the charge for the spinning process. The distance between the cathode (static fiber collection point) and anode (tip of capillary needle) was 15 cm with pump rate maintained at 1 mL/h. The flow rate was, however, increased to 2 mL/h in the case of the polystyrene/phthalocyanine composite to avoid clogging of the needle.

2.3. Equipment

Scanning electron microscope (SEM) images of the fiber alone or in the presence of LuTPPc were obtained using a JOEL JSM 840 scanning electron microscope. The fiber diameters were measured using Cell^D software from Olympus. The average diameter of seventy different fibers was taken.

Raman data was obtained using a Bruker Vertex 70-Ram II spectrometer equipped with a Nd:YAG laser that emit at 1064 nm and liquid nitrogen cooled germanium detector.

The GAUSSIAN 03 programme [29] running on an Intel/Linux cluster was used to perform DFT calculations. The calculations were

done at the B3LYP/6-31G(d) level for geometry optimization and excited energy calculations (TDDFT). All visualization used the GAUSSVIEW 4.1 program.

2.4. Singlet oxygen quantum yield determination of LuTPPc in the fiber mat

A chemical method was employed for the determination of the singlet oxygen quantum yield of the LuTPPc or ZnPc modified fibers in water. The singlet oxygen quantum yield (Φ_{Δ}) determinations were carried out in aqueous solutions using ADMA as the quencher (absorbance ~ 0.542 at 380 nm). The modified fiber, LuTPPc (or ZnPc)/polystyrene (10 mg) was suspended (as small pieces) in this solution and irradiated using a set-up consisting of a General Electric Quartz lamp (300 W), 600 nm glass (Schott) and water filters, to filter off ultra-violet and far infrared radiations respectively. An interference filter at 670 nm with bandwidth of 40 nm was placed in the light path just before the cell containing the sample. The ADMA quantum yield Φ_{ADMA} was calculated using Eq. (1), while the extinction coefficient of ADMA in water has been reported as $\log(\epsilon) = 4.1$ [30].

$$\Phi_{ADMA} = \frac{(C_0 - C_t)V_R}{I_{abs}t} \quad (1)$$

where C_0 and C_t are the ADMA concentrations prior to and after irradiation, respectively; V_R is the solution volume; t is the irradiation time per cycle and I_{abs} is defined by Eq. (2).

$$I_{abs} = \frac{\alpha I}{N_A} \quad (2)$$

where $\alpha = 1 - 10^{-A(\lambda)}$, $A(\lambda)$ is the absorbance of the sensitizer at the irradiation wavelength, A is the irradiated area (2.5 cm^2), I is the intensity of light ($4.52 \times 10^{16} \text{ photons cm}^{-2} \text{ s}^{-1}$) and N_A is Avogadro's constant.

The absorbance used for Eq. (2) is that of the LuTPPc (or ZnPc) on the fiber (not in solution) measured by placing the fiber on a glass plate. The light intensity measured refers to the light reaching the spectrophotometer cell, and it is expected that some of the light may be scattered, hence the Φ_{Δ} value of the LuTPPc (or ZnPc) on the fiber is an estimate. The UV–Vis spectrum of the modified fiber was obtained by placing it directly on the glass plate using a Shimadzu UV-2550 spectrophotometer.

The singlet oxygen quantum yields Φ_{Δ} were calculated using Eq. (3) [31]

$$\frac{1}{\Phi_{ADMA}} = \frac{1}{\Phi_{\Delta}} + \frac{1}{\Phi_{\Delta}} \cdot \frac{k_d}{k_a} \cdot \frac{1}{[ADMA]} \quad (3)$$

where k_d is the decay constant of singlet oxygen and k_a is the rate constant of the reaction of ADMA with $O_2(^1\Delta_g)$. The intercept obtained from the plot of $1/\Phi_{ADMA}$ versus $1/[ADMA]$ gives $1/\Phi_{\Delta}$.

2.5. Photocatalytic reactions

Photocatalytic reactions were carried out in a magnetically stirred batch reactor (glass vial). The irradiation experiments were carried out using the photolysis set-up described above for singlet oxygen detection. The intensity of the light reaching the reaction vessel was measured with a power meter (POWER MAX 5100, Molelectron Detector Inc) and found to be $3.5 \times 10^{20} \text{ photons cm}^{-2} \text{ s}^{-1}$. The transformation was monitored by observing the absorption bands of 4-chlorophenol after each photolysis cycle of 15 min using a Shimadzu UV-2550 spectrophotometer. The experiments were carried out using a variety of concentrations of 4-chlorophenol in pH 11 phosphate buffer. Each sample solution contained 10 mg of functionalized fiber.

2.6. Chromatographic analysis

The photolysis products were separated and analyzed using both gas chromatography (GC) and by direct injection into ion trap mass spectrometer fitted with an electrospray ionization (ESI-MS) mass source. In the case of the gas chromatographic analyses, an Agilent Technologies 6820 GC system fitted with a DB-MS Agilent J & W GC column was employed. A Finnigan MAT LCQ ion trap mass spectrometer equipped with an electro-spray ionization (ESI) source was used for mass analysis. Spectra were acquired in the negative ion mode, with the capillary temperature set at 200 °C and sheath gas set at 60 arbitrary units, with the capillary and tube lens voltage set at –20 and –5 V, respectively. The aqueous photocatalysed sample solution was extracted with dichloromethane and then injected into the GC.

3. Results and discussion

3.1. Microscopic and spectroscopic characterization of the LuTPPc/PS fiber

The characterization of the ZnPc/PS was the same as for LuTPPc/PS so only the latter will be discussed. LuTPPc is not aggregated in organic media as reported before [27].

3.1.1. Elemental analyses – consistency of composition

Since LuTPPc has a relatively smaller size and much more conducting compared to the polystyrene, a separation of the composite during the electrospinning process similar to what has been observed in gel electrophoresis was possible [32]. This would result in fibers at different stages of the electrospinning process having different compositions, with fiber at the first stage of electrospinning having higher phthalocyanine content than those at later stages. In order to assess the uniformity in composition of the fiber during the different stages of its formation from the mixture of polystyrene and phthalocyanine, three samples of the fiber were collected at different stages of the electrospinning process and analyzed using elemental analyses. The elemental compositions are given in Table 1. The nitrogen content in the mixture was overshadowed by the high carbon and hydrogen content in the polystyrene and the phthalocyanine. However, the fibers have generally the same composition and are expected to show reproducible behavior in any application. Thus elemental analyses results confirm that there was no separation of the LuTPPc and fiber during synthesis. One important deduction from the elemental analysis is the fact that the molecules of the phthalocyanine and the polystyrene have interacted strongly through their π - π electrons of the aromatic systems.

3.1.2. Scanning electron microscopic (SEM) images

Cylindrically shaped fibers of polystyrene alone and the polystyrene/LuTPPc composite were formed. Characteristic features of the fibers were examined using scanning electron microscopy (SEM) to assess fiber morphology. Both LuTPPc/PS and PS fibers did not form appreciable amount of beads under the above experimental conditions and consist of mostly long unbranched strands of cylindrical fibers as shown in Fig. 2.

Table 1
Elemental composition of samples of LuTPPc composite fiber.

| Sample | Element | | |
|---------|---------|-------|------|
| | C | H | N |
| Ps–Pc 1 | 92.00 | 7.621 | – |
| Ps–Pc 2 | 92.39 | 7.533 | – |
| Ps–Pc 3 | 92.19 | 7.627 | 0.03 |

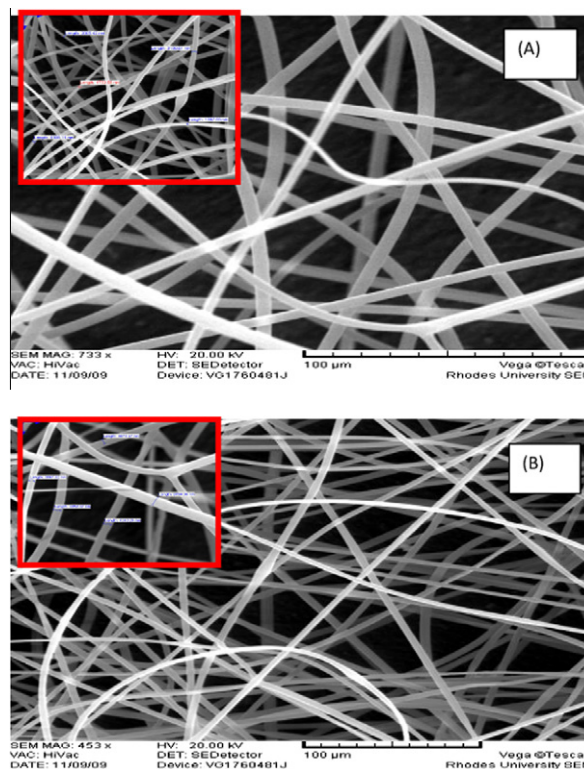


Fig. 2. Fiber mat of (A) polystyrene alone and (B) LuTPPc/polystyrene composite at 100 µm resolution and insert is 50 µm resolution.

The average diameter of the polystyrene fiber alone was found to be $2.72 \pm 0.40 \mu\text{m}$, using Cell[^]D software from Olympus. There was a slight increase in average fiber diameter to $4.73 \pm 0.51 \mu\text{m}$ in the presence of LuTPPc.

The fiber diameters of the polystyrene alone ranged from 1.8 to 3.2 µm. These fiber diameters were thinner than those obtained (3.52–4.09 µm) by Pai et al. [33], using DMF alone as solvent, instead of THF:DMF solvent mixture in this work. This is expected because higher concentration of the polymer in the solvent, 30% was used in Ref. [33], while polymer concentration of 25% was used in the present case. This observation is consistent with theory which predicts that the fiber diameter depends allometrically on solution viscosity [34,35].

3.1.3. Raman spectra

The Raman spectral studies were done in order to ascertain electronic interactions between the polymer and the phthalocyanine. Interpretation of these spectra has been aided by the theoretical spectrum of the pure polystyrene polymer. The density functional theory (DFT) calculations were carried out on a subunit of polystyrene polymer. Fig. 3A shows the theoretical (a) and experimental (b) Raman spectra of the polystyrene alone.

As indicated in Fig. 3A, there is a good correlation between the theoretically obtained spectra and the experimental one. The peaks between 2500 and 3000 cm^{-1} are attributed to stretches due to the aromatic ring of the PS [36], and are consistent with the theoretical calculations. To determine any electronic interaction between the polystyrene and the phthalocyanine, the Raman spectrum of the composite fiber (LuTPPc/PS) was taken and compared with that of the polymer alone as depicted in Fig. 3B. The observed changes in the peak shapes of the LuTPPc/PS composite, Fig. 3B(b) compared to PS alone, Fig. 3B(a) suggest that the phthalocyanine is interacting with the polystyrene aromatic system. This might be due to the strong π - π interactions of the phthalocyanine and polystyrene aromatic systems.

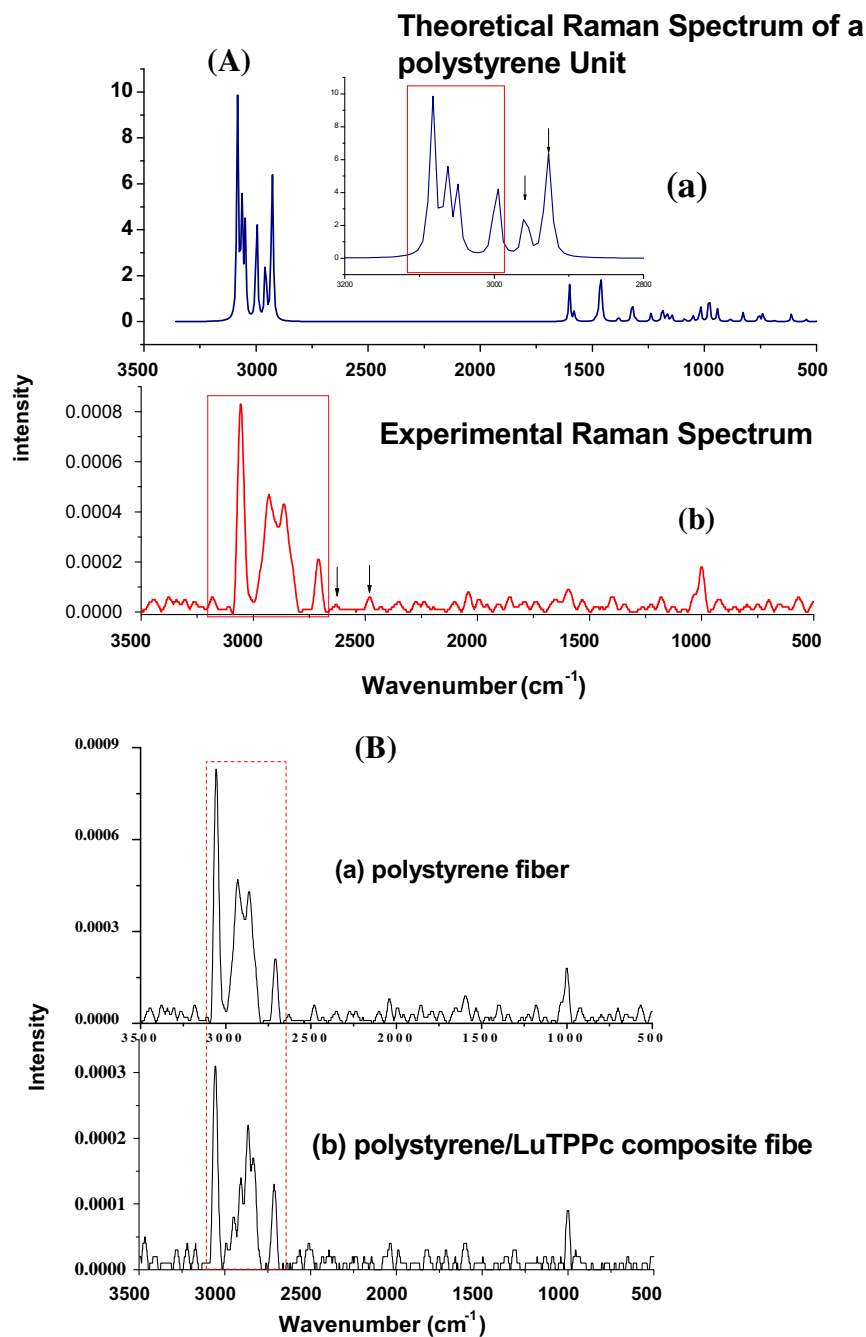


Fig. 3. (A) Theoretical (a) and experimental (b) Raman spectra of polystyrene and (B) Raman spectra of (a) polystyrene and (b) polystyrene/LuTPPc composite fibers.

3.1.4. UV–Vis absorbance spectra

Fig. 4 shows the electronic absorption spectrum of the LuTPPc in THF together with the solid state electronic spectra of phthalocyanine, polystyrene fiber and that of the LuTPPc/PS composite fiber. The spectra of the solids were recorded from the fiber (or LuTPPc/PS) or LuTPPc alone fixed on a glass slide.

As shown in Fig. 4a, the electronic spectrum of LuTPPc shows a Q-band absorption maximum of 690 nm in solution. The solid state electronic spectrum of the phthalocyanine alone, Fig. 4b shows broadening. When more than one Pc macrocycles are close to each other, whether they are chemically bonded or not, the transition dipole moments can couple (exciton coupling) to cause drastic spectral changes particularly in the Q-band region. Depending on the conformation between the chromophores, shifts of the Q-band

(generally to the blue, while to the red in less common cases), splitting and/or broadening can be observed [37]. The red-shifts of the Q-band have mostly been observed in the solid-state phase where the chromophores are aligned in a slipped-cofacial manner (the degeneracy of Q band is lifted in this arrangement) and can be rationalized in terms of exciton coupling. The differences in the solid state and solution spectra phthalocyanines have been reported by other workers [38]. Aggregation in the solid state however does not favor generation of singlet oxygen.

In Fig. 4c, the non-functionalized polystyrene fibers show no obvious absorption band. However for LuTPPc/PS, the Q-band absorption is relatively broader and more red-shifted (6 nm) compared to that of the phthalocyanine in THF solution, but less red shifted compared to solid LuTPPc, Fig. 4d. It could also be deduced

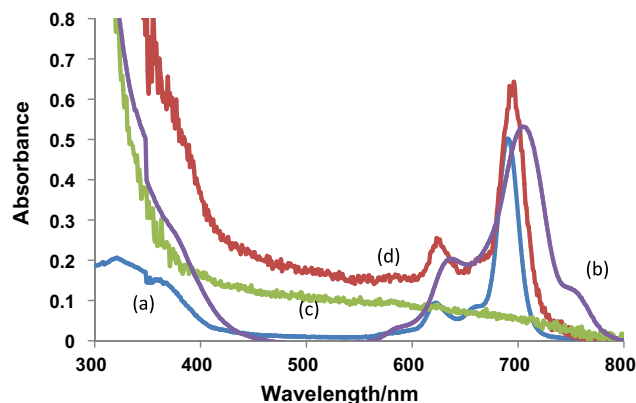


Fig. 4. UV-Vis absorbance spectra of: (a) 3.8×10^{-6} M LuTPPc in THF solution, (b) solid LuTPPc, (c) polystyrene fiber, (d) polystyrene/LuTPPc composite fiber.

from Fig. 4d, that the phthalocyanine is uniformly dispersed within the fiber matrix, since there is less broadening (hence less aggregation) compared to solid LuTPPc.

For further evidence of a uniform dispersal of the LuTPPc on the fiber matrix and for possible quantitative applications of the functionalized polystyrene fiber, the electronic spectra of various packing of the fiber were obtained as in Fig. 5. As shown, there is considerable quantitative correlation between the amount of phthalocyanine on the fiber, since doubling the thickness of the fiber on the glass substrate, almost doubles the LuTPPc absorbance. This observation also suggests that the composite fiber is uniform in composition.

Leaching has been reported [39] to be a major problem associated with the application of these functionalized polymer fibers in various solvent media. In this work, an attempt has been made to find a suitable solvent in which the functionalized polystyrene could be applied with minimal or no leaching of the phthalocyanine from the fiber. It was observed that in purely hydrocarbon based solvents such as hexane; there was no leaching or very minimal leaching of the Pc, Fig. 6b and c. Similarly there was no leakage of the Pc in water, Fig. 6a, hence it is employed in this work for the degradation of 4-chlorophenol in water. However, in some organic solvents there is considerable leaching or even a complete dissolution of the fiber to liberate the phthalocyanine. A typical

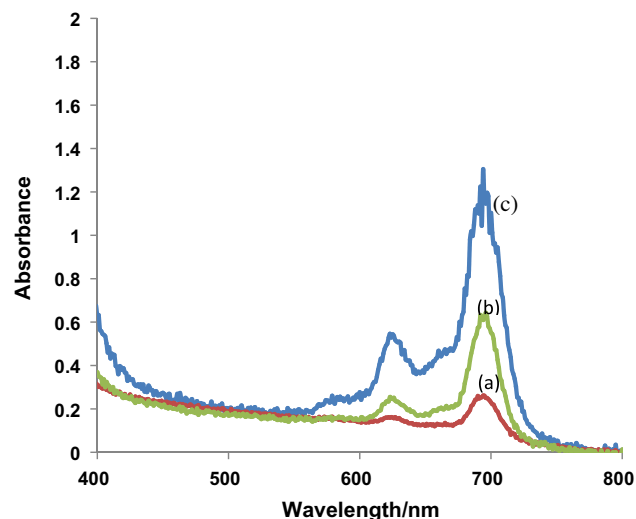


Fig. 5. Variation of absorbance of the polystyrene/LuTPPc composite fiber with fiber mat thickness $r \approx 0.1$ cm placed on glass plate: (a) r , (b) $2r$, (c) $4r$.

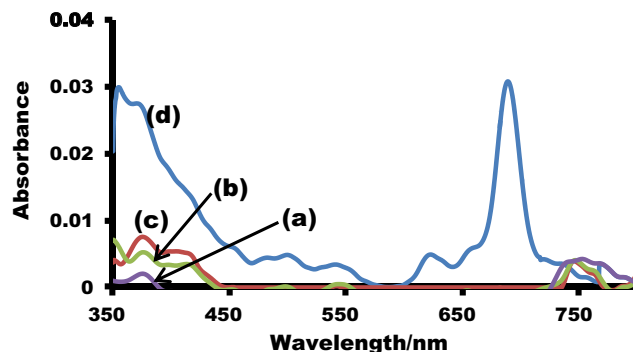


Fig. 6. UV-Vis spectra in water, THF and hexane after immersing the functionalized fiber in them for various time intervals (a) 1.8 h in water, (b) 4 h in hexane, (c) 12 h in hexane, (d) momentarily in THF.

case involving THF is shown in Fig. 6d. However, the fact that the Q band is observed in THF, confirms that the integrity of the phthalocyanine is maintained in the fiber, Fig. 6d. The lack of leaching in water is important for real applications of the fibers in aqueous media as is the case in this work.

3.2. Singlet oxygen quantum yield of LuTPPc (and ZnPc) in functionalized fiber

Since the functionalized fibers are intended for use in an aqueous medium, singlet oxygen quantum yield of the phthalocyanine in the functionalized fiber was determined in water by employing ADMA, a singlet oxygen quencher. Fig. 7 shows the spectral changes of ADMA upon irradiation indicating that the functionalized fiber is capable of generating singlet oxygen. The quantum yield was estimated to be 0.22 and 0.13 for LuTPPc/PS and ZnPc/PS, respectively, suggesting the possibility of the conjugates being used in the photo-conversion of 4-chlorophenol in aqueous media. The lower singlet oxygen quantum yield of ZnPc/PS compared to LuTPPc/PS could be attributed to the heavy atom effect of the Lu in the latter which encourages intersystem crossing hence larger singlet oxygen quantum yields. The presence of bulky groups in LuTPPc would also prevent aggregation, enhancing singlet oxygen quantum yield.

When the pure polystyrene polymer fiber was used under similar conditions, no degradation of ADMA was observed since phthalocyanine is responsible for the singlet oxygen generation within functionalized fiber.

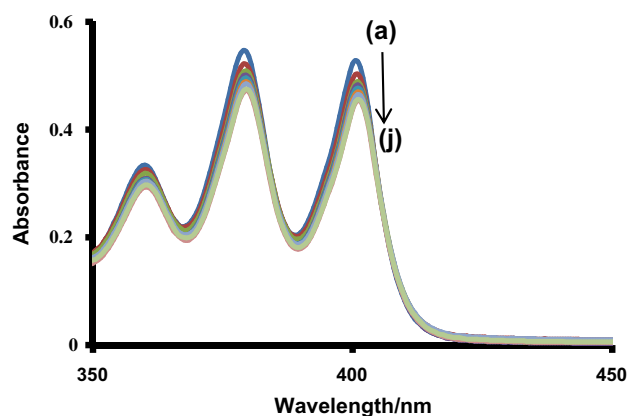


Fig. 7. UV-Vis spectral changes observed on photolysis of 10 mg LuTPPc/polystyrene fiber in the presence of ADMA in water. (a) starting spectrum of ADMA, (j) spectrum after 20 min of photolysis, starting ADMA concentration = 5.53×10^{-5} mol dm^{-3} , irradiation interval = 2 min.

3.3. UV–Vis spectral changes during degradation of 4-chlorophenol

Studies of the photocatalysed degradation of 4-chlorophenol (4-CP) using the LuTPPc (or ZnPc)/polystyrene fiber, were carried out at a pH of 11 to enhance the deprotonation of 4-chlorophenol, since its pKa value is 9.34. It has been reported that the deprotonated form of 4-chlorophenol, is more oxidizable by singlet oxygen than in its protonated or neutral form [40,41]. Fig. 8 shows the electronic absorption spectral changes observed on photolysis 4-chlorophenol using LuTPPc/PS. The 4-chlorophenol peaks at 243 nm and 297 nm decrease in intensity during irradiation of the sample in the presence of the functionalized fiber. This suggests conversion of the 4-chlorophenol to photolysis products. This is supported by the emergence of two new absorbance bands, observed at 227 and 280 nm which increase in intensity with time, Fig. 8 (inset). The increase is clearer for the peak at 227 nm since it is more resolved. These peaks are similar to what has been reported for the degradation of 4-CP in the presence of phthalocyanines and other photosensitizers [10]. The absorption peak at 227 nm could be assigned to benzoquinone while that at 280 nm to hydroquinone [42–44]. When the pure polystyrene polymer fiber was used as control, no spectral changes of the aqueous 4-chlorophenol solution were observed. Thus suggesting that LuTPPc in the functionalized fiber was involved in the photo-conversion of the 4-chlorophenol. When ZnPc/PS was employed, spectral changes similar to those in Fig. 8 were obtained though a longer time (30 min) was required for a significant change.

There was no leaching of LuTPPc from the composite fiber into the aqueous solution of 4-chlorophenol. This was apparent from the fact that there was no Q-band absorption corresponding to the phthalocyanine in the UV–Vis spectra of sample solution during photocatalysis. Thus the polystyrene polymer fiber serves as good support system. Also the Pc is not soluble in water.

It has been reported [42] that the formation of *p*-benzoquinone is mainly due to the reaction of singlet oxygen with 4-chlorophenol (Type II mechanism, Eqs. (4)–(6), Scheme 1), while the formation of hydroquinone and other dimeric products are explained by an electron transfer reactions involving the phthalocyanine, oxygen and 4-chlorophenol (Type I mechanism, Eqs. (7)–(11), Scheme 2). We investigated the type of mechanism involved by conducting the photolysis in an oxygen saturated solution and in a solution containing sodium azide, a singlet oxygen quencher. The production of *p*-benzoquinone at 227 nm was quite enhanced in the oxygen saturated solution, while drastically reduced in the azide saturated solution, thus supporting the Type II mechanism

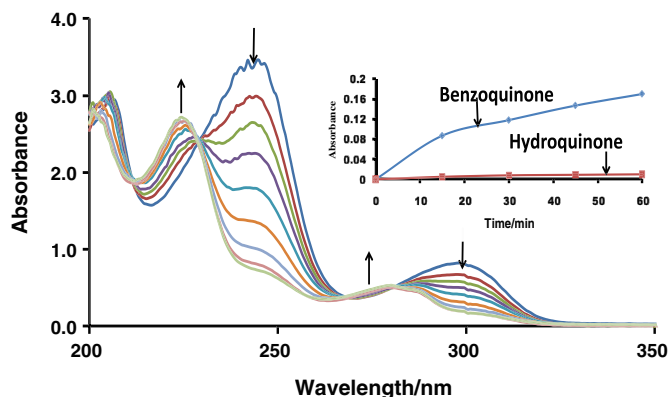
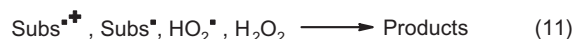
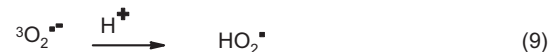


Fig. 8. Electronic absorption spectral changes of 3.58×10^{-4} mol L⁻¹ 4-CP during its visible light photocatalysis in the presence of 10 mg LuTPPc/polystyrene functionalized fiber. The spectra were recorded 15 min intervals. Insert: plot of absorbance vs. time for the two peaks.



Scheme 1. Type II mechanism. Subs = substrate.



Scheme 2. Type I mechanism. Subs = 4-CP.

proposed for its formation. Production of the hydroquinone under the above conditions was not affected all. Also when a free radical scavenger, tert-butyl alcohol, was used, hydroquinone was not produced. Thus the functionalized fiber is capable of degrading 4-chlorophenol via both the proposed Type II and Type I mechanisms, which starts with the photogeneration of singlet oxygen and radicals, respectively, by the immobilized phthalocyanine. Such dual photodegradative routes have been reported for a sulphonated cobalt phthalocyanine anchored on MCM-41, a mesoporous molecular sieve, for the degradation of 2,4-dichlorophenol [45].

3.4. Kinetics of 4-chlorophenol oxidation

The initial pollutant concentration is of immense importance in any water treatment. The photodegradation (or phototransformation) of 4-CP using the LuTPPc (or ZnPc)/polystyrene fiber showed first order kinetics (Fig. 9 for LuTPPc/PS) as observed before for the photodegradation of 4-chlorophenol using sulphonated phthalocyanine complex of aluminum [46] and degradation of 2,4-dichlorophenol by sulphonated cobalt phthalocyanine immobilized on a mesoporous molecular sieves, (MCM-41) [45] as well as the heterogeneous photodegradation of 4-nitrophenol using suspension of TiO₂ [47].

Reaction rates, rate constants and half-lives were evaluated from Fig. 9 (and are listed Table 2). The observed rate constant (k_{obs}) decreased with an increase in concentration as expected. The values of k_{obs} listed in Table 2 for LuTPPc/PS are larger than those reported using sulfonated phthalocyanines in aqueous media under homogeneous photocatalytic oxidation of 4-CP [46], which were of the order of 10^{-3} min⁻¹ on average and larger than for ZnPc/PS. Thus the LuTPPc/polystyrene fiber shows better photocatalytic behavior towards photocatalytic oxidation of 4-CP than ZnPc/PS.

The half-lives of the photo-degradation of 4-chlorophenol by the LuTPPc/PS, within the experimental concentrations, are quite comparable to the values reported for other chlorinated phenols [45], but far shorter than those of ZnPc/PS. Equally encouraging is the fact that these half-lives are within one and half hours of photo-irradiation for LuTPPc/PS, suggesting that the functionalized fiber is a promising fabric that could be applied for real life removal of chlorophenols in aquatic systems.

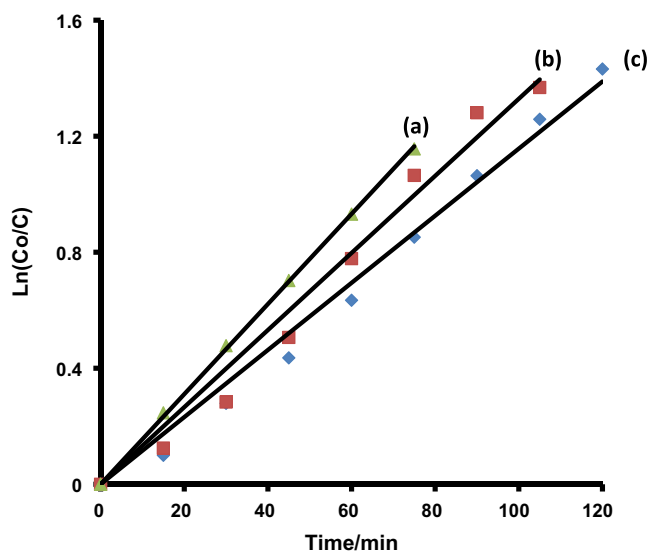


Fig. 9. Effect of initial concentration of 4-chlorophenol on its rate of degradation. Concentrations were monitored at 243 nm. Starting concentrations (a) $2.72 \times 10^{-4} \text{ mol L}^{-1}$, (b) $3.58 \times 10^{-4} \text{ mol L}^{-1}$ and (c) $4.36 \times 10^{-4} \text{ mol L}^{-1}$. Amount of functionalized fiber 10 mg.

Table 2

The rate, rate constant (k_{obs}) and half-life ($t_{1/2}$) of various initial concentrations of 4-chlorophenol using LuTPPc/PS. Values in brackets are when ZnPc/PS is employed.

| Concentration/ $\times 10^{-4} \text{ mol L}^{-1}$ | $k_{\text{obs}}/\text{min}^{-1}$ | Initial rate/ $\times 10^{-6} \text{ mol L}^{-1} \text{ min}^{-1}$ | Half-life/min |
|---|----------------------------------|---|----------------|
| 1.56 | 0.0231(0.0006) | 3.60(0.094) | 30.00(1155.25) |
| 2.72 | 0.0155(0.0005) | 4.22(0.136) | 44.72(1386.30) |
| 3.58 | 0.0133(0.00045) | 4.76(0.161) | 52.12(1540.33) |
| 4.04 | 0.0123(0.00042) | 4.97(0.169) | 55.45(1650.35) |
| 4.36 | 0.0116(0.00041) | 5.06(0.179) | 59.75(1690.60) |
| 5.06 | 0.0101(0.00038) | 5.11(0.192) | 68.63(1824.07) |

The Langmuir-Hinshelwood rate expression was also used to describe the relationship between the initial rate of degradation of 4-chlorophenol and the corresponding initial concentration. This model, Eq. (12), has successfully been applied to describe the kinetics of solid-liquid reactions. In particular, it has been applied in heterogeneous photocatalytic degradation reactions [48]. A linear expression can conveniently be obtained by plotting the reciprocal of the initial rate against the reciprocal of the initial concentration, Eq. (12).

$$\frac{1}{\text{rate}} = \frac{1}{k_a} + \frac{1}{k_a K C_0} \quad (12)$$

where k_a is the apparent reaction rate constant, K is the adsorption coefficient and C_0 corresponds to the initial concentration of 4-chlorophenol.

In this work, we obtained a reasonable linear fit (for the plot of $1/\text{rate}$ versus $1/C_0$) with a non-zero intercept and a correlation coefficient of 0.9767, Fig. 10. The results presented in Fig. 10 (for LuTPPc/PS) give an indication that the Langmuir-Hinshelwood (L-H) kinetic model is an appropriate model in describing the kinetics of the photo-degradation of 4-chlorophenol by our heterogeneous catalytic system based on the phthalocyanine complex of lutetium functionalized on polystyrene polymer fiber. A similar plots as shown in Fig. 10 was also obtained for ZnPc/PS. Therefore it could be said that the catalysis occurs appreciably at the surface of the functionalized fiber.

From the intercept in Fig. 10, the apparent rate constant k_a was determined to be $6.39 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$ for LuTPPc/PS and

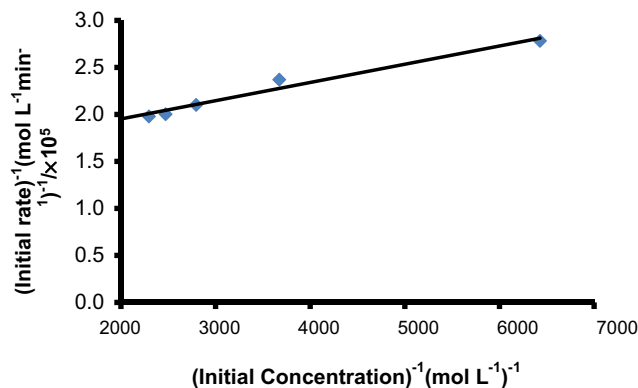


Fig. 10. Plot of the inverse of initial reaction rate (rate^{-1}) vs. the reciprocal of the initial concentration of 4-Cp for photooxidation using 10 mg LuTPPc/polystyrene functionalized fiber.

$3.3 \times 10^{-7} \text{ mol L}^{-1} \text{ min}^{-1}$ for ZnPc/PS, indicating faster reaction kinetics for the degradation of 4-chlorophenol with LuTPPc/PS fiber than with ZnPc/PS fiber. Additionally, the adsorption coefficient, K was found to be $0.81 \text{ mol}^{-1} \text{ L}$ for LuTPPc/PS and $2.48 \times 10^3 \text{ mol L}^{-1}$ for ZnPc/PS. The value of adsorption coefficient is less than one ($K < 1$), in the case of LuTPPc/PS, suggesting that adsorption was less favored compared to desorption while the converse is true for ZnPc/PS fiber.

3.5. Gas chromatographic analysis

The reaction products were further identified using chromatography. This was done by spiking sample solutions with standard solutions of the products. As shown in Fig. 11, the photo-degradation products consist of benzoquinone and hydroquinone, confirming what was predicted based on the UV spectral peaks of the product solutions, (Fig. 8). However a third product was also observed which could not easily be identified using standards of other possible photo-degradation products of 4-chlorophenol.

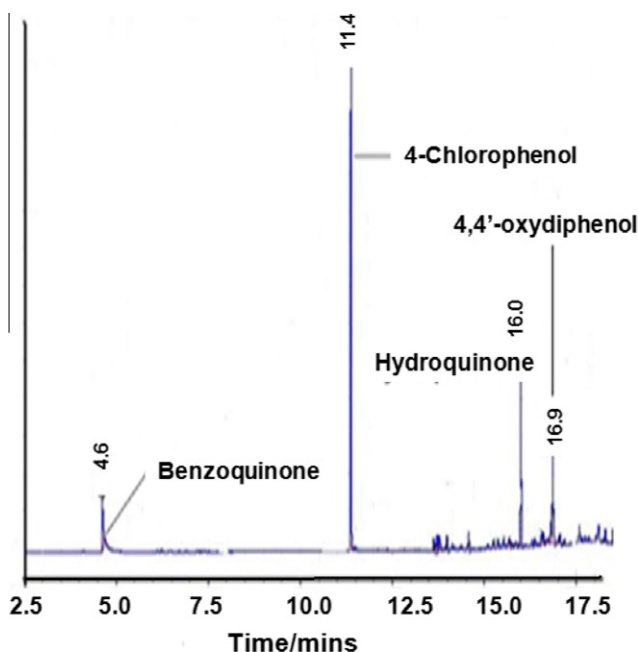


Fig. 11. Gas chromatographic traces of $3.58 \times 10^{-4} \text{ M}$ 4-chlorophenol after being photolyzed 12 h in the presence of 10 mg LuTPPc/polystyrene functionalized fiber.

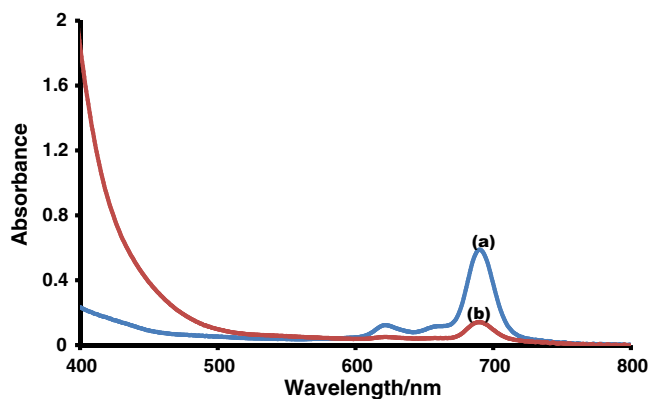


Fig. 12. UV–Vis spectra of 10 mg of LuTPPc/polystyrene functionalized fiber (a) not used in catalysis, (b) used in catalysis (Time 12 h), each dissolved in 4 ml of THF.

Thus mass spectrometry (MS) was further used in this regard. The following molecular ions corresponding to the products were identified; $[M-H^+]=109$ amu for hydroquinone and $[M-2H^+]=200$ amu for a dimeric form of hydroquinone, 4,4'-dihydroxydiphenol. The same products were obtained for ZnPc/PS.

It might appear at first sight, as depicted in Fig. 11, that the quantitative degradation of 4-chlorophenol by the functionalized fiber is not a competitive process. However, when one considers the amount of fiber used and, for that matter, the amount of LuTPPc (or ZnPc), used, this compares favorably with other cases of photo-degradation of chlorophenols using phthalocyanines [45,46].

3.6. Fate of LuTPPc during photocatalysis

The photostability of imbedded sensitizers is an important factor for the application of such a fabric for photocatalysis. Therefore the photostability of LuTPPc within the fiber matrix was assessed by observing the Q-band absorption of an equivalent amount (10 mg) of the fiber before and after catalysis, both dissolved in equal volume of THF (4 mL), Fig. 12. As indicated, the decrease in the absorption band of LuTPPc after the photolysis suggests that the phthalocyanine photo-degrades upon continuous irradiation for 12 h. This could also equally account for the incomplete degradation of the 4-chlorophenol as in indicated by the gas chromatogram in Fig. 11. Replacement of the functionalized fiber during photolysis may be required. ZnPc/PS showed almost complete degradation after this time.

4. Conclusion

In this report, we have demonstrated that a polystyrene polymer fiber functionalized with tetraphenoxo phthalocyanine complex of lutetium is capable of degrading 4-chlorophenol in the presence of visible light, with a better efficiency than ZnPc/PS. The products obtained suggest that the degradation is both of Types I and II reaction mechanisms. The reaction follows first order kinetics with half-lives that are within one and half hours for LuTPPc/PS, suggesting that it is a viable method. However there was an appreciable degradation of phthalocyanine during prolonged irradiation for 12 h.

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