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Photocatalytic transformation of chlorophenols under homogeneous and heterogeneous conditions using palladium octadodecylthio phthalocyanine

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ABSTRACT

Homogeneous and heterogeneous photosensitized transformations of 4-chlorophenol (4-CP) and pentachlorophenol (PCP) using palladium octadodecylthiophthalocyanine (PdODPc) were investigated. Under heterogeneous conditions, the photosensitizer was supported on functionalized single walled carbon nanotubes (SWCNTs). Homogeneous photosensitization proved to be more effective than the heterogeneous reaction in terms of percentage of transformation achieved. The kinetics of heterogeneous catalysis proved that ads-PdODPc–SWCNT–COOH (where SWCNT has been functionalized with COOH groups) was reusable for 4-CP while its activity degenerated when reused for PCP. Singlet oxygen was confirmed as playing an active role in the reactions.

1. Introduction

The environmental pollution by chlorophenols has been well documented [1–3]. There has been considerable investigation of degradation of phenols using oxidants in the presence of catalysts such as metallophthalocyanines (MPcs). Using oxidants has proved successful with chlorophenols (and related molecules) degraded to less harmful products such as CO_2 [4–10]. However, processes involving no oxidants are still preferred.

Due to their high absorption in the visible region and singlet oxygen generating ability, MPc complexes have been used as homogeneous and heterogeneous photocatalysts [11–15]. In spite of the advantage of ease of catalyst regeneration associated with heterogeneous catalysis, homogeneous catalysis holds the potential for kinetic studies of the photodegradation reactions and easier understanding of the mechanisms involved in the reaction.

Open-shell metallophthalocyanines produce large triplet state quantum yields and efficiently generate singlet oxygen [16], which is the initiator of Type II reactions found to be the dominant pathway in photosensitized degradations or transformations. In Type II mechanism the triplet state of the photosensitizers (^{3}MPc*) transfers energy to the ground state molecular oxygen ($^3O_2$) to give energetic singlet oxygen ($^1O_2$), Eq. (1), which in turn oxidizes the substrate (Subs), Eq. (2).

$$^3\mathrm{MPc}* + {}^3\mathrm{O}_2 \rightarrow {}^1\mathrm{O}_2 \quad (1)$$

$$^1\mathrm{O}_2 + \mathrm{Subs} \rightarrow \mathrm{Oxidationproducts} \quad (2)$$

In addition to their singlet oxygen generating abilities, open-shell metallo phthalocyanines (e.g. PdPc and PtPc) show high photostability [17,18] which is also an advantage over other metallophthalocyanines. This has made them prime candidates for photosensitization reactions. PdPc and PtPc derivatives have been reported to photosensitize oxidation reactions of 4-nitrophenol (4-NP) under homogeneous conditions [19]. A PdPc complex containing long alkyl chains was found to give high quantum yields for the phototransformation of 4-NP, hence it is employed in this work for the phototransformation of chlorophenols under homogeneous and heterogeneous conditions [20]. SWCNTs were chosen as support in heterogeneous catalysis because of ease of immobilization of MPcs due to the strong π–π interaction between SWCNTs and MPc complexes.

Thus this work investigates the photosensitizing properties of (2,3,9,10,16,17,23,24-octakis(dodecylthiophthalocyaninato) palladium(II) (PdODPc, Fig. 1) for the phototransformation of 4-chlorophenol and pentachlorophenol under homogeneous and heterogeneous conditions. For the latter, the PdPc complex was adsorbed on single walled carbon nanotubes (SWCNT).

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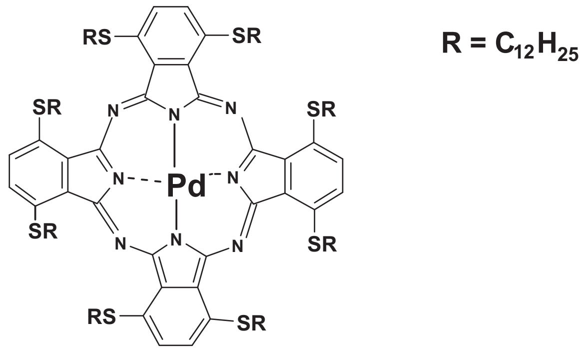

Fig. 1. Molecular structure of the photosensitizer (PdODPc) employed in this work.

2. Experimental

2.1. Materials

4-Chlorophenol (4-CP), pentachlorophenol (PCP), 2,3,5,6-tetrachloro-1,4-benzoquinone and hydroquinone were purchased from SAARCHEM. Dichloromethane (DCM) (SAARCHEM) was distilled before use. Distilled deionized water was used to prepare basic aqueous solutions of chlorophenols. Single walled carbon nanotubes (SWCNT, 0.7–1.2 nm in diameter and 2–20 μm in length) obtained from Aldrich were purified as reported in the literature [21], and briefly described in Section 2.2. Diethylamine and NaOH were used to increase the pH of organic and aqueous media respectively. Anthracene-9,10-bis-methylmalonate (ADMA) was from Sigma–Aldrich. The synthesis of the photocatalyst: 2,3,9,10,16,17,23,24-octakis (dodecylthio-phthalocyaninato) palladium(II) (PdODPc, Fig. 1) has been reported before [22].

2.2. Purification and functionalization of SWCNTs

SWCNTs were purified (oxidized) to form SWCNT–COOH by adding the raw SWCNTs (100 mg) to a mixture of HNO_3 and H_2SO_4 (3:1) [21] The resulting suspension was stirred at a temperature of 70 °C for 2 h. The final mixture was cooled to room temperature and washed with excess millipore water until a pH of 5 was obtained. The purified SWCNTs (SWCNT–COOH) were dried in an oven for 12 h.

2.3. Immobilization of PdODPc on SWCNT–COOH

The PdODPc (Fig. 1) complex was dissolved in DCM to give an absorbance of approximately 1 and 50 mg SWCNT–COOH was added and the mixture was stirred until there was no change in absorbance of the MPc. The mixture was centrifuged and the supernatant decanted, leaving the particles of SWCNT–COOH and the PdODPc adsorbed on their surface (represented as ads-PdODPc–SWCNT–COOH). The particles were washed with distilled deionized water, methanol and acetone and then air-dried for 24 h. The concentration of adsorbed MPcs was calculated from the differences in absorbances to be 1.0×10^{-8} M.

2.4. Equipment

X-ray powder diffraction patterns were recorded on a Bruker D8, Discover equipped with a proportional counter, using Cu-Kα radiation (λ = 1.5405 Å, nickel filter). Data were collected in the range from $2\theta = 5^\circ$ to 60°, scanning at $1^\circ\ \text{min}^{-1}$ with a filter time-constant of 2.5 s per step and a slit width of 6.0 mm. Samples were placed on a silicon wafer slide. The X-ray diffraction data were treated using Eva (evaluation curve fitting) software. Baseline correction was performed on each diffraction pattern by subtracting a spline fitted to the curved background and the full-width at half-maximum values used in this study were obtained from the fitted curves.

Bruker Vertex 70-Ram II Raman spectrometer (equipped with a 1064 nm Nd:YAG laser and a liquid nitrogen cooled germanium detector) was used to collect Raman data. The Raman spectral data for the SWCNT–COOH, PdODPc, ads-PdODPc–SWCNT–COOH were obtained from their powdered samples.

2.5. Photochemical methods

Irradiation experiments were carried out with a tungsten lamp (100 W, 30 V) perpendicular to the direction of measurement. A 600 nm glass cut off filter (Schott) and a water filter were used to filter off ultraviolet and infrared radiations, respectively. An interference filter (Intor, 670 nm with a band width of 40 nm) was additionally placed in the light path before the sample, to ensure the excitation of the Q band only.

The intensity of the light reaching the reaction vessel was measured with a power meter (POWER MAX 5100, Molectron Detector Inc.) and was found to be 1×10^{15} photons $\text{cm}^{-2}\,\text{s}^{-1}$. The degradations of the analytes were monitored through their absorption peaks after each photolysis cycle on a Shimadzu UV-2550 UV–Vis spectrophotometer. A 1 cm pathlength UV–Vis spectrophotometric cell, fitted with a tight fitting stopper was used as the reaction vessel. For homogeneous reactions, experiments were carried out in DCM in which both the MPc and chlorophenols dissolved, while for heterogeneous reactions, experiments were carried out in aqueous media, using a suspension of PdODPc adsorbed on SWCNT–COOH. The photocatalysis products were analyzed using an Agilent Technologies 6820 GC system (HP 5973, using a HP-1 column). The participation of $^1O_2$ in the photolysis was confirmed by the addition of sodium azide, (a singlet oxygen quencher) to the photolysis reaction media. Singlet oxygen involvement was further confirmed by bubbling argon into the reaction media.

2.6. Photocatalysis parameters

2.6.1. Homogeneous reactions

The quantum yields of phototransformation of chlorophenols (Φ_{CP}) was calculated using Eq. (3) [23].

$$\Phi_{\text{CP}} = \frac{[C_0 - C_t]V}{I_{\text{abs}}t} \tag{3}$$

where C_0 and C_t are the concentrations of chlorophenols before and after irradiation respectively; V is the volume of the sample in the cell; t is the irradiation time. I_{abs} is given by Eq. (4)

$$I_{\text{abs}} = \frac{\alpha A I}{N_A} \tag{4}$$

where $\alpha = 1 - 10^{-A(\lambda)}$ ($A(\lambda)$ is the absorbance of the sensitizer at the irradiation wavelength), A is the irradiated area (3.14 cm^2), I is the intensity of light (1×10^{15} photons $\text{cm}^{-2}\,\text{s}^{-1}$) and N_A is Avogadro's constant.

Assuming the transformation of chlorophenols follows Type II reaction pathway, the three processes involved in the phototransformation of chlorophenols are represented by Eqs. (5)–(7).

$$^1O_2 \xrightarrow{k_d} {}^3O_2 \tag{5}$$

$$\text{CP} + {}^1O_2 \xrightarrow{k_q} {}^3O_2 \tag{6}$$

$$\text{CP} + {}^1O_2 \xrightarrow{k_a} \text{Products} \tag{7}$$

The rate constants involved are for the decay of $^1O_2$ (k_d, Eq. (5)), physical quenching of $^1O_2$ by the substrate (k_q, Eq. (6)) and the formation of oxidation products (k_a, Eq. (7)). Using Eqs. (5)–(7), the