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Platinum 1,10-phenanthroline: Photosensitizer for photocatalytic degradation of 4-chlorophenol

Ahmed Kadry Aboul-Gheit[a,*], Sahar Moustafa Ahmed[a], Doaa Samir El-Desouki[a],
Samira Mohamed Abdel-Azeem[a] and Mohamed Fathy El-Shahat[b]

[a] *Egyptian Petroleum Research Institute, Cairo, EG-11787, Egypt*
[b] *Chemistry Department, Faculty of Science, Ain Shams University, Cairo, EG-11787, Egypt*

**Corresponding author at: Egyptian Petroleum Research Institute, Cairo, EG-11787, Egypt. Tel.: +202.22729100; fax: +202.747433.*
E-mail address: aboulgheit2000@hotmail.com (A.K. Aboul-Gheit).

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ABSTRACT

It is more economic to apply photodegradation of organic pollutants in presence of the visible light irradiation (sunlight) than applying more costfull ultraviolet lamps. Hence, platinum 1,10-phenanthroline complex has been prepared and tested as a photosensitizer for photodegrading 4-chlorophenol in water, which has been found almost completely achieved (98.5 %) after three hours of visible irradiation. Nevertheless, irradiation at 364 and 254 nm exhibits lower efficiencies. At visible irradiation, the platinum complex gives the highest activation of singlet state oxygen formation ($^1O_2$) compared to 364 and 254 nm irradiation as supported by electron para-magnetic resonance data. On the other hand, the behavior of formation and disappearance of photodegradation intermediates: hydroquinone, benzoquinone, hydroxybenzoquinone, using the platinum complex applying the three current irradiations are found to supports these findings. However, organic acids have accumulated as a function of irradiation time and hence considered to be rate-controlling.

1. Introduction

Over the past four decades, dye-sensitized solar cells and related systems have been extensively investigated [1-5] because of their low cost and high performance as sensitizers as well as their favorable light absorption, redox properties, luminescence emission, and excited-state lifetime and their photostability [6–9]. 1,10-phenanthroline is the parent of an important class of chelating agents. It is a well-known bidentate chelating ligand having distinct properties enabling it to function as a triplet-state photosensitizer, especially in complexes with lanthanides [10]. Nevertheless, uncoordinated 1,10-phenanthroline existing in a metal complex is quite rare [11,12]. The direct irradiation of chlorophenols in water generates more toxic organic compounds (like the polychlorinated dibenzo-p-dioxines) than the parent compound. Also, the semiconductor, TiO_2 widely used as a photocatalyst for the mineralization of chlorophenols which absorbs in the ultraviolet region where only approximately 4% of solar radiation is effective [13]. To overcome these disadvantages, photosensitizers, which strongly absorb in the visible region, are preferred. Shukla *et al.*, [14] studied Pt(1,10-phenanthroline)$^{2+}$ photosensitizers for the generation of $^1O_2$ and found that the ability of these complexes to photosensitize the production of $^1O_2$ depends on nature of the ligands attached to platinum(II). Singlet molecular oxygen, $^1O_2$, is one of the most active intermediates involved in photosensitized oxygen reactions in chemical and biological systems [15,16]. The generation of singlet oxygen by a photoactivated sensitizer usually takes place by the transfer of energy from the triplet state of the photosensitizer to molecular oxygen. This energy transfer as well as the relaxation of the involved states was described by the standard model [17]. In the present work, we investigated the photodegradation of 4-chlorophenol (4-CP) using Pt(1,10-phenanthroline)Cl_2 complex as a photosensitizer (catalyst) under three different irradiations (254, 364 or 400-800 nm).

2. Experimental

2.1. Preparation of dichloro(1,10-phenanthroline) platinum(II) complex

Dichloro(1,10-phenanthroline)platinum(II) complex was prepared by adding a solution of $H_2PtCl_6.6H_2O$ (50 mL) and 1,10-phenanthroline (0.1 g) in 150 mL distilled water then reflux for 20 h. The reaction mixture was allowed to cool to the room temperature, then the precipitated light yellow product that was filtered out, washed with water, and dried under vacuum. The yield was 1 g (94% purity) which decomposed at 360 °C [18].

2.2. Photocatalytic degradation reaction

The effect of wavelength variation in photolysis of 4-chloro phenol was investigated using three lamps, two of them irradiate at 254 and 364 nm. The third light lamp range was between 400-800 nm.

The photocatalytic degradation reaction was carried out via irradiating 300 mL of an aqueous solution containing 300 ppm of 4-chlorophenol with the ultraviolet (UV) or the visible (VIS) light. A continuous current of air was bubbled in the solution in

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presence of the powdered catalyst (0.5 g/L pollutant solution). At varying time intervals, samples of the irradiated solution were withdrawn for analysis. The 4-CP and its photodegradation intermediates were extracted from water via solid phase extraction on Porapak Q packed into a 10 cm x 1/8 inch Teflon column using methanol as eluent, followed by gas chromatography analysis using a capillary Porapak Q column [19-21]. The standard intermediates were purchased from Aldrich (USA).

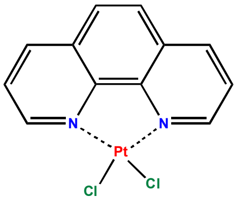
2.3. Instrumentation

The qualitative infrared absorption spectra (FTIR) of the prepared Pt phenanthroline complex was conducted using ATI Mattson Infinity Series TM, Bench top 961 controlled by win first TM V2.01 software. (Egyptian Petroleum Research Institute “EPRI”). The NMR spectra of the phenanthroline and its Pt complex were measured in deuterated chloroform using trimethyl silane (TMS) as internal reference using a 200 MHZ signal Varian JEMINI spectrometer. The NMR spectra were measured in Micro analytic Center, Cairo University. Electron Para magnetic resonance (EPR) measurements were carried out using AJEOL JES-TE 100 ESR spectrometer for the detection of singlet oxygen which is produced from the reaction using a quencher (2,2,6,6-tetramethyl-4-piperidinol) in DMF. The reaction mixture was placed into a narrow quartz tube and placed in the EPR cavity for measurements. The TEM photograph was done using Jeol TEM-1200 EXII.

3. Results and discussion

3.1. Characterization of the dichloro(1,10-phenanthroline) platinum(II) complex

The reaction between 1,10-phenanthroline and hexachloroplatinic acid gives a yellow product [Pt(1,10-phenanthroline)dichloride] which was characterized by elemental analysis, FT-IR and ^{1}H NMR spectroscopy. The elemental analysis of the synthesized square planer complex indicated a single 1,10-phenanthroline ligand per one platinum atom as well as two chloride ion ligands and showed 98.0 % purity. The complex structure is accordingly given in Scheme 1.



Scheme 1

The co-ordination of the phenanthroline ligand to platinum through the two nitrogens was supported by the presence of phenanthroline in FT-IR spectrum (not given) of the complex. The square planar co-ordination was supported by presence of a major band at 349 cm^{-1} and a smaller shoulder at 330 cm^{-1} assigned to the symmetric and asymmetric Pt–Cl stretching from the two chloro ligands [22]. The bands at 694 cm^{-1} and 697 cm^{-1} were due to Pt-N in pyridine ring and 1581 cm^{-1} for C-N$_{Ar}$.

^{1}H NMR spectrum obtained for the phenanthroline Pt complex (Figure 1a) shows two doublets in aromatic region at 9.29 ppm (d, 2H) and 9.09 ppm (d, 2H) assigned to protons at positions of the complex. The ^{1}H NMR spectrum of 1,10-phenanthroline molecule (Figure 1b) shows two doublets at 8.69 ppm (d, 2H) and 8.49 ppm (d, 2H). The resulting chemical shift due to Pt complex co-ordination is 0.6 ppm. It is clear that the N-N co-ordination of phenanthroline to the Pt occurs. The preferential co-ordination of phenanthroline through the two nitrogen atoms rather than through the ortho-quinoline system was also expected on the basis of the greater basicity of the diminic system with respect to the quinoline functionality [22-24].

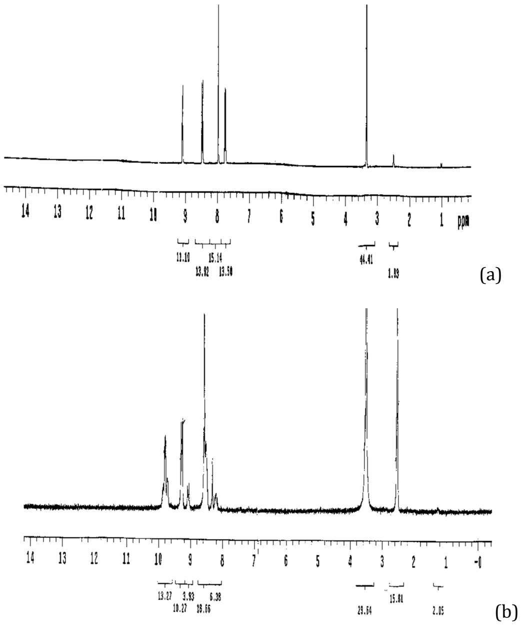


Figure 1. ^{1}H NMR for (a) unloaded 1,10- phenanthroline and (b) 1,10-phenanthroline Pt complex.

3.1.1. Electron para-magnetic resonance (EPR) for 1,10-phenanthroline Pt-complex

The ability of these complexes to photosensitize the production of $^1O_2$ depends on the nature of the ligands attached to platinum (II) [14]. Singlet molecular oxygen $^1O_2$ is one of the most active intermediates involved in photosensitized oxygen reactions in chemical systems [15,16,25]. The generation of singlet oxygen by a photoactivated sensitizer usually takes place by the transfer of energy from the triplet state of the photosensitizer to molecular oxygen. In this work, the photooxidation of 2,2,6,6-tetramethyl-4-piperidinol (NH) by $^1O_2$ which is produced via excitation of our photosensitizer [(Pt(phen)Cl$_2$ complex] has been used as a quencher and gives stable nitroxide (NO$^•$) free radicals [14,26]. We evaluated the amount of free radical via recording its intensity on Varian E-12 EPR spectrometer using an aqueous EPR cell. Figure 2 (a and b) shows that there is an almost linear relationship between irradiation time and the intensity of free radicals generated during applying the 254, 364 and 400-800 nm irradiations. Evidently, the highest intensity has resulted using the visible irradiation, whereas the lowest intensity is obtained using the 254 nm irradiation. The transmission electron microscopy (TEM) photograph of the Pt(1,10-phenanthroline complex) is given in Figure 3. It shows that the Pt particles fall in the nano-size dimension (4-7 nm), which confirms the successful preparation of the current complex.

3.1.2. Photodegradation of 4-chlorophenol in water using the Pt(1,10-phenanthroline complex) as a photosensitizer irradiated at 254, 364 and 400-800 nm

The behavior of 4-CP degradation using the 254, 364 and 400-800 nm irradiations in presence of the 1,10-phenanthroline Pt complex as a catalyst is depicted in Figure 4.

Evidently, the activity of photodegradation is highest using the visible light irradiation but lowest using the UV irradiation range, which emphasizes the effectiveness of the complex as a photosensitizer. In other words, the energy transfer starts with the excitation of the sensitizer by irradiation with visible light, which involves generation of the highly oxidative singlet oxygen species responsible for the destruction of organic pollutants [13,27].

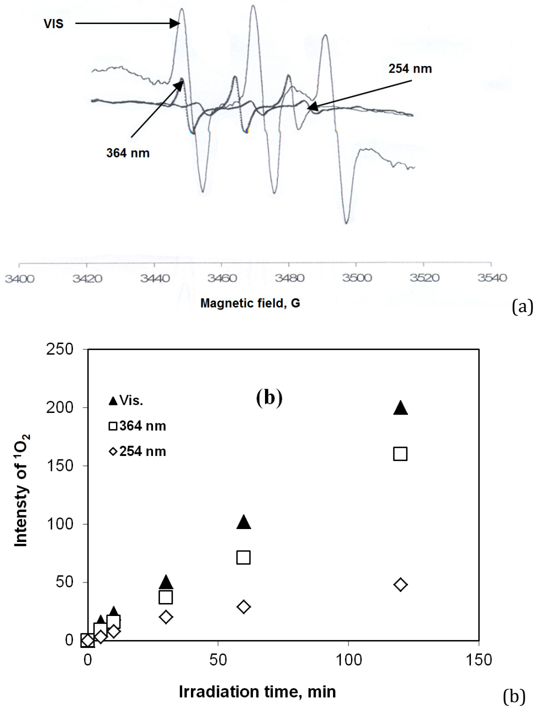


Figure 2. (a) Intensity of oxygen in singlet state, (b) EPR diagram of Pt complex at different irradiation sources.

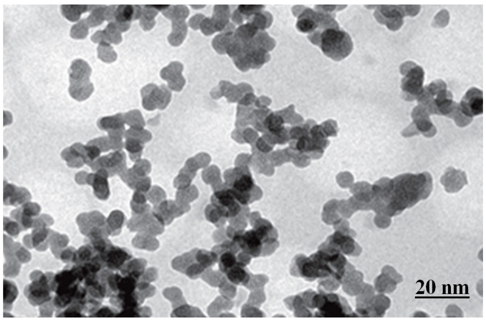


Figure 3. TEM photograph of Pt phenanthroline complex.

To evaluate the magnitude of the photocatalytic degradation activity of the Pt complex (as a photosensitizer) under the three current irradiations, the 1st order kinetics is applied and given in Figure 5a and 5b. These data show that k_1 (during the low irradiation time range 0-15 min), is always higher than k_2 (during the time range 15-180 min). k_1 amounts to 0.0391, 0.0490 and 0.0651 min^{-1} using 254, 364 nm and visible light, respectively. In the 15-180 min range, k_2 for this reaction amounts to 0.0101, 0.0176 and 0.0177 min^{-1}, respectively. The almost equal values of k_2 using 364 nm and visible irradiations can be attributed to the high visible content irradiated by the 364 nm lamp. The deviation of k_2 from first order kinetics at irradiation periods longer than 15 min can be attributed to accumulation of the intermediates thus decreasing the photodegradation rate. This decrease would be compensated if the initial concentration of the pollutant (CP) in water is decreased than 300 ppm. Moreover, using the photosensitizer in an unsupport form would also contribute to such deviation of k_2.

The stability of phenanthroline Pt complex under study has been examined after 180 min run using the three irradiation lamps (254, 364 and 400-800 nm) and was found to encounter very slight change (±1% after 180 min).

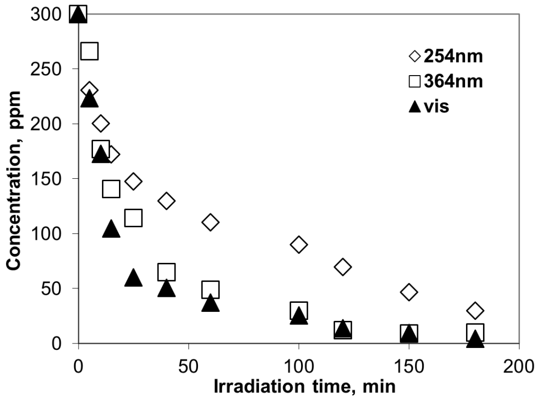


Figure 4. Photocatalytic degradation of 4-CP as a function of irradiation time using Pt complex.

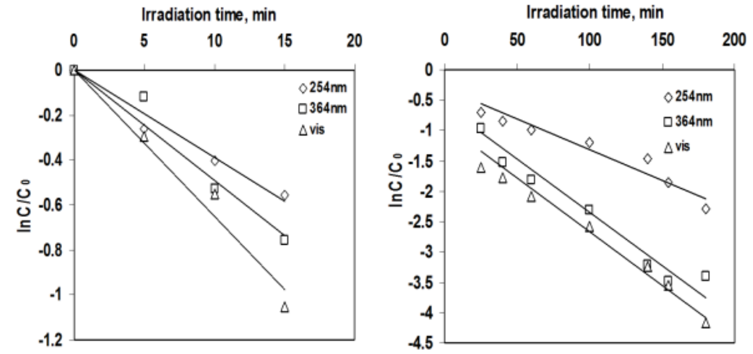
4-CP photodegradation intermediates: Benzoquinone (BQ) and hydroquinone (HQ) have been assumed [28] to be primary photodegradation products of 4-CP, whereas hydroxybenzo quinone (HBQ) is a secondary photodegradation product. All cyclic intermediates will then degrade forming organic acids as depicted in Scheme 2. In the present work, we support this assumption by the results in Figure 6a, 6b and 6c where maximum BQ is 101.1, 83.4 and 13.7 ppm at 60 min irradiation using the 254, 364 and 400-800 nm, respectively. However, the maximum production of HQ is 38.2 ppm at 150 min using 254 nm irradiation and 4.6 ppm at 25 min using the 364 nm irradiation but it is absent using the visible irradiation. It is evident that both HQ and BQ are produced in more significant quantities via irradiation with the lower wavelength lamp (254 nm).

$$\text{4-CP} \rightarrow \text{HQ} \rightarrow \text{BQ} \rightarrow \text{HBQ} \rightarrow \text{Organic acids}$$

Scheme 2

HBQ which is a secondary intermediate as proposed by Theurich *et al.* and Czaplicka [29,30], also, this product is found in the present work to be the highest using the visible light irradiation (48 ppm at 60 min), but somewhat lower using the 364 and 254 nm irradiation. HBQ is the last cyclic intermediate in the photodegradation sequence; it cracks and suffers ring opening producing organic acids (Figure 6a, 6b and 6c).

Organic acids are found to increase with increasing the irradiation time up to 180 min using the 254 nm irradiation. Nevertheless, using the 364 and visible irradiations (Figure 6b and 6c), these acids increase to a maximum of 106.8 ppm at 150 min and 101.4 ppm at 100 min, respectively, beyond which these acids decline with a further increase of irradiation time, indicating that these visible–containing irradiations activated bond-rupturing more than the purely UV (254 nm) irradiation by virtue of activating the singlet oxygen state formation (Figure 2). This degradation of acids is evidently slow indicating that these acids are strongly resistive against photodegradation, most probably due to their lower electron density compared to the other intermediates which possess aromatic nature. Hence, these acids (aliphatics) degradation can be considered the rate controlling step in presence of 1,10-phenanthroline Pt complex catalyst.



(a) (b)

Figure 5. First order plot for (a) the initial irradiation period 0-15 min and (b) the 15-180 min irradiation period of 4-CP photodegradation using Pt complex.

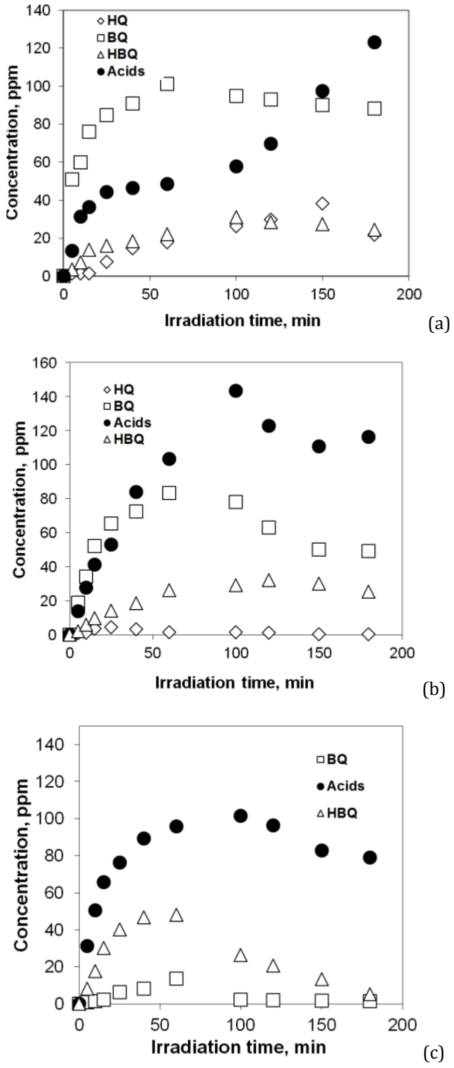


Figure 6. Intermediates in 4-CP photodegradation using (a) 254 nm, (b) 364 nm and (c) 400-800 nm irradiation using Pt-complex as a photosensitizer.

4. Conclusions

The catalyst (photosensitizer) used in this work is Pt(1,10-phenanthroline) complex has been prepared and its structure confirmed via FT-IR and ^{1}H NMR. The photodegradation of 4-chlorophenol using Pt(1,10-phenanthroline) complex as a photosensitizer in water has been achieved under three irradiation wavelengths 254, 364 nm and visible and was found to be in the order: VIS > 364 nm > 254 nm. During the initial (0-15 min) period of irradiation at all wavelengths investigated, the rate constant is higher than that obtained during the longer irradiation period. The intermediates produced during the course of photodegradation of 4-CP are BQ, HQ and HBQ. The data show that BQ is the highest intermediate at 254 and 364 nm irradiations but the lowest at the visible irradiation. HQ is the lowest intermediate at 254 and 364 nm but absent at the visible irradiation. Organic acids are increased as a function of irradiation period using 254 and 364 nm but decrease beyond 100min at the visible irradiation. Nevertheless, this behavior shows that the rate of acids photo-removal is the rate controlling step in the overall photodegradation of 4-CP.

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