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Photophysical and photochemical properties of a water-soluble perylene diimide derivative☆

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Abstract

The absorbance maximum of synthesized water soluble perylene 4-carboxylphenyl-*bis*-diimide (PECA) is found to be about 50 nm lower in water, as compared to absorbance in organic solvents, and the singlet energy is 61.4 kcal mol^{-1} in aqueous solutions, compared to 54.4 kcal mol^{-1} in organic solvents. The fluorescence quantum yields were similar in both media but radiative and fluorescence lifetimes are found to be enhanced about twice (τ_f from 8 to 15 ns), and the rate of fluorescence is decreased twofold in aqueous solution, as compared to organic solutions. PECA is proven to produce reactive superoxide anion and/or hydroperoxy radical in aqueous solutions, in the pH range of 6–12 ($\phi_{O_2^{\bullet-}}^{PECA} = 0.062$ at pH=9). The superoxide/hydroperoxy formation is found to be enhanced in the presence of ferric ions ($\phi_{O_2^{\bullet-}}^{PECA} = 0.10$ at pH=9). The quantum yield of fluorescence emission, Q_f, was measured to be 1.00 at pH 11.85, and 0.87 at pH 6.60. The difference is attributed to an aggregation effect due to low solubility in neutral aqueous solution. Fluorescence quenching by Co^{+2} ions has yielded a quenching rate of 2.3×10^{12} M^{-1} s^{-1} for perylene diimide. The degradation of bromacil and 2,4-dichlorophenoxyacetic acid (2,4-D) pesticides in neutral aqueous solutions has proven that PECA/Fe^{+3} solar photocatalyst is as reactive as singlet oxygen in photo oxidations for organic pollutants. High thermal and photo stabilities and the regain of catalysts on precipitation, are the advantages with respect to classical triplet organic photosensitizers (methylene blue, rose bengal, etc.) employed for singlet oxygen photodegradations. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

A photo energy transfer mechanism from a triplet photo-sensitizer pigment to oxygen is known to produce singlet oxygen [1]. Degradation of organic and biological contaminants is solely dependent on the reactivity of singlet oxygen. Organic dyes with low triplet energy levels (below 35 kcal mol^{-1}, such as methylene blue, rose bengal type, tetraphenyl porhyrine) are known to produce singlet oxygen under solar irradiation through a photo energy-transfer process. The lifetime of singlet oxygen in water is reported to be 2 µs, which is 10-fold to 100-fold less than in organic phases. However sufficient reactivities are observed toward organic compounds and living bacteria in aqueous phase [1–3]. The generation and the reactivity of singlet oxygen is pH dependent in the aqueous phase and it is most reactive between pH values 7 and 10, the maximum reaching at about pH 9. Singlet oxygen solar detoxification and disinfection of contaminated waters are proven to be effective on disinfection but insufficient in detoxification when numerous types of organic contaminants are present [4,5].

Perylene diimides are known to be excellent thermal- and photo-stable sensitizers [6]. Absorption in the visible region (450–530 nm) enables them for use in solar applications. Energy and electron transfer processes proceed through singlet states. They are capable of reacting as an electron acceptor as well as electron donor [6,7]. Fluorescence quantum yields of unity and high energy difference between singlet–triplet states, 54–27 kcal mol^{-1}, respectively, are taken as evidence of singlet state photo processes [8,9].
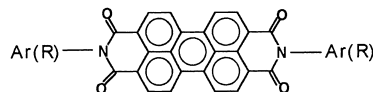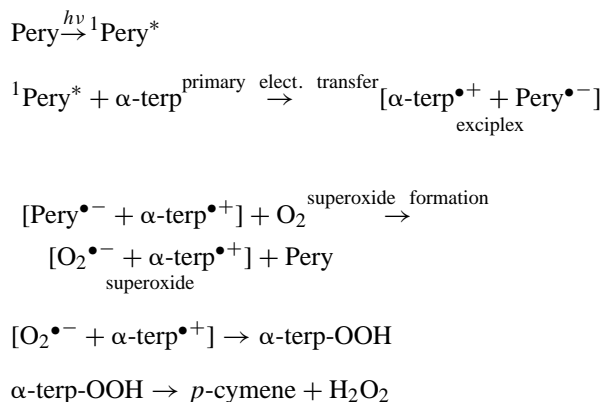
Recent studies on the photochemical reaction of perylene *bis*-diphenylimide derivative with α-terpinene olefin, have proven that perylene diimide anion radical forms an exciplex [10,11]. As seen in the scheme below, photosensitized oxygenation proceeds by an electron transfer from exciplex to oxygen, that results in the formation of superoxide anion radical [10,11]:

$$\text{Pery} \xrightarrow{h\nu} {}^1\text{Pery}^*$$

$${}^1\text{Pery}^* + \alpha\text{-terp} \xrightarrow[]{\text{primary}\quad\text{elect.}\quad\text{transfer}} \underbrace{[\alpha\text{-terp}^{\bullet+} + \text{Pery}^{\bullet-}]}_{\text{exciplex}}$$

$$[\text{Pery}^{\bullet-} + \alpha\text{-terp}^{\bullet+}] + \text{O}_2 \xrightarrow{\text{superoxide}\quad\text{formation}}$$
$$\underbrace{[\text{O}_2^{\bullet-} + \alpha\text{-terp}^{\bullet+}]}_{\text{superoxide}} + \text{Pery}$$

$$[\text{O}_2^{\bullet-} + \alpha\text{-terp}^{\bullet+}] \rightarrow \alpha\text{-terp-OOH}$$

$$\alpha\text{-terp-OOH} \rightarrow p\text{-cymene} + \text{H}_2\text{O}_2$$

Superoxide would give oxygenated products, in part similar to singlet oxygen reactions. Quantum yield of formation of superoxide is expected to be low. But the quantum yield of the above reactions with α-terpinene olefin in acetonitrile is reported to be high enough, 0.4, for the complete conversion of α-terpinene to p-cymene in minutes [10,11]. A water soluble derivative of perylene diimide, 4-carboxylphenyl perylene diimide (PECA), is synthesized for the determination of photophysical and photochemical properties of perylene diimides in aqueous phases and for comparison of these reactivities in aqueous solutions.

2. Experimental details

2.1. Organic synthesis

2.1.1. Perylene 4-carboxylphenyl-bis-diimide [12]

Ethyl 4-aminobenzoate, 500 mg, 3 mmol, was dissolved in a mixture of 50 ml *m*-cresol and 0.9 ml of isoquinoline. The mixture was stirred at 80°C for 1 h under nitrogen atmosphere. Perylene dianhydride, 390 mg, 1 mmol, was added in three portions into the solution of ethyl 4-aminobenzoate and stirring under nitrogen atmosphere was continued for 3 h at 80°C. The temperature was first raised to 120°C and kept for 2 h, and then raised to 220°C and kept for 48 h with stirring. The solution was poured into 250 ml of acetone after cooling down. The precipitate was filtered and first washed with 10% sodium hydroxide solution to remove impurities, later with distilled water and dried under vacuum. A yield of 440 mg, 64% of perylene ethyl 4-carboxylatephenyl-*bis*-diimide (EPECA) $C_{42}H_{26}N_2O_8$, MW: 686.68 g mol^{-1}, was obtained. Molecular structure was analyzed. Micro analysis: Found (Calculated) % C: 73.23 (73.46), % H: 3.75 (3.81); IR (in KBr) $\nu^{-C=O}$ cm^{-1}:

1740, 1755, 1770; UV (in chloroform) λ nm (ε): 459 (24 700), 490 (58 100), 527 (91 600). UV data of EPECA presents characteristic absorptions of perylene diimides [6,8]. EPECA (345 mg, 0.5 mmol) was poured into 50 ml 10% sodium hydroxide, methanol was added with mixing until observing a dark red suspension. The mixture was refluxed for less than an hour, prior to observation of green colour that indicated the imide ring opening to amide form. Completion of hydrolysis of ester was noticed by the conversion of dark red colour of suspension to light pink-red colour. The mixture was acidified, the precipitate filtered and washed with distilled water. Dried product yielded 161 mg, 51%, $C_{38}H_{18}N_2O_8$, MW: 630.64 g mol^{-1}, PECA. Molecular structure was analyzed, IR (in KBr) ν^{CO-OH} cm^{-1}: 3300–2950, $\nu^{-C=O}$ cm^{-1}: 1702, ν^{-imide} cm^{-1}: 1662; ^{1}H NMR (in DMSO-d$_6$/pyridine-d$_5$) δ ppm: 8.43 (Ar–H, dd, J_1=overlapped, J_2=7.8 Hz), 8.50 (Ar–H, dd, J_1=overlapped, J_2=7.8 Hz), 7.84–7.88 (Ph–H, m), 11.91 (COOH, s); UV (in CHCl$_3$) λ nm (ε): 458 (12 700), 490 (39 600), 527 (60 300); UV (in H$_2$O, pH=7–8) λ nm (ε): 407 (1720), 438 (3600), 466 (4640). Solubility in water was found to be about 10^{-4} M above pH 8, and decreased to about 10^{-6} M at pH 5. The solubility in dimethylsulfoxide was detected to be about 3 times higher than in chloroform ($\sim 10^{-5}$ M). All the other perylene diimide derivatives were synthesized as reported earlier [8].

2.1.2. 9,10-Anthracene-dipropionic acid [13]

Anthracene (9.0 g, 51 mmol) was dissolved in 70 ml anhydrous dioxane and paraformaldehyde (8.5 g, 28 mmol), 12 ml concentrated HCl was added. The solution was refluxed for 5 h and stirred at room temperature overnight. Yellow precipitate was filtered and washed with dioxane. Dried product yielded 7.2 g, 51% 9,10-dichloromethylanthracene, $C_{16}H_{12}Cl_2$, MW: 275.12 g mol^{-1}, m.p.: 254°C. Molecular structure was analyzed, ^{1}H NMR (in CDCl$_3$) δ ppm: 5.62 (–CH$_2$–, s), 7.65 and 7.68 (Ar–H, dd, J_1=3.2 Hz, J_2=7.0 Hz), 8.38 and 8.41 (Ar–H, dd, J_1= 3.2 Hz, J_2=7.0 Hz), IR (in KBr) ν^{Ar-H} cm^{-1}: 769 (bending). Sodium metal (1.2 g, 52 mmol) was dissolved in warm 50 ml p-xylene, and diethyl malonate (16.5 ml, 150 mmol) was added. The solution was refluxed for 10 min and 9,10-dichloromethylanthracene (7.0 g, 25 mmol) was added and an additional 4 h reflux was performed, on cooling yellow crystals precipitated. Excess p-xylene was distilled out, precipitate was washed with distilled water and re-dissolved in xylene for crystallization. Dried crystals yielded 6.3 g, 48%, ethyl 9,10-anthracenedimethyl-2-malonate, $C_{30}H_{34}O_8$, MW: 522.60 g mol^{-1}, m.p.: 172°C. Molecular structure was analyzed. Micro analysis: Found (Calculated): % C: 68.88 (68.96), % H: 6.30 (6.56); ^{1}H NMR (in CDCl$_3$) δ ppm: 1.05 (CH$_3$–, t, J=7.0 Hz), 4.06 (–CH$_2$O–, q, J=7.0 Hz), 3.85 (–CH–, t, J=7.3 Hz), 4.31 (Ar–CH$_2$–, d, J=7.3 Hz), 7.51 and 7.55 (Ar–H, dd, J_1=3.2 Hz, J_2=7.0 Hz), 8.31 and 8.35 (Ar–H, dd, J_1=3.2 Hz, J_2=7.0 Hz); IR (in KBr) $\nu^{C=O}$ cm^{-1}: 1735,

ν^{Ar-H} cm^{-1}: 2853 (stretching), 756 (bending). A solution of ethyl 9,10-anthracenedimethyl-2-malonate (5.3 g, 10 mmol), sodium hydroxide (6.8 g, 170 mmol), 46 ml ethanol, and 23 ml water was refluxed for 3 h on a water bath. Acidification with HCl resulted in formation of tetracarboxylic acid derivative, that has precipitated out as a yellowish amorphous mass. Precipitate was washed with water and crystallized in ethanol, yielded 3.5 g, 88%, tetra carboxylic acid (9,10-anthracenedimethyl-malonic acid), $C_{22}H_{18}O_8$, MW: 396.27 g mol^{-1}, m.p.: 251–253°C. 9,10-Anthracenedimethyl-malonic acid (3.5 g, 9 mmol) was dissolved in 25 ml diphenylether and refluxed (at b.p. 259°C of diphenyl ether) for 3 h. Carbon dioxide gas was evolved from the solution during reflux. Precipitation was observed on cooling to room temperature. Hot sodium hydroxide 15%, was added into the stirred solution until whole of the precipitate was dissolved. pH was adjusted to 5.5–6.0 with dilute HCl and the precipitate was filtered, crystallized from ethanol–water mixture. A yield of 1.2 g, 41%, 9,10-anthracene-dipropionic acid (ADPA), $C_{20}H_{18}O_4$, MW: 322.36 g mol^{-1}, m.p.: 244°C was obtained. Molecular structure was analyzed. Micro analysis: Found (Calculated): % C: 74.17 (74.52), % H: 5.85 (5.63); ^{1}H NMR (in DMSO-d_6) δ ppm: 2.63 (–CH$_2$–C=O, t, J=8.2 Hz), 3.86 (Ar–CH$_2$–, t, J=8.2 Hz), 7.58 and 7.60 (Ar–H, dd, J_1=3.2 Hz, J_2=7.0 Hz), 8.35 and 8.37 (Ar–H, dd, J_1=3.2 Hz, J_2=7.0 Hz); IR (in KBr) $\nu^{C=O}$ cm^{-1}: 1689, ν^{Ar-H} cm^{-1}: 2900 (stretching), 750 (bending).

2.2. Spectroscopic analysis

Synthesized compounds were analyzed on a Perkin Elmer 1600 FTIR spectrophotometer for IR spectroscopy, a UV-1601 Shimadzu and JASCO V-530 UV–VIS spectrophotometer for UV–Vis spectroscopy, at Bruker AC 200L 200 MHz NMR for NMR spectroscopy and a Carlo Erba elemental analyzer instrument for micro analysis. Fluorescence emission spectra were recorded on a PTI QM1 fluorecence spectrophotometer. Solvents that are used for UV and emission spectroscopy investigations, were methanol, acetonitrile or chloroform supplied by Merck in UV grade. Fluorescence quantum yield of PECA was measured with reference to absorption and fluoresence emission of fluorescein in 0.1 M NaOH solution, λ_{exc}=499 nm. Fluorescein and CoCl$_2\cdot$6H$_2$O were supplied by BDH and Merck "rein" grade, respectively, and were used without any further purification. Superoxide quantum yields were measured with reference to fluorescein in sodium borate buffer solution at pH 9. Borate solution was used for having a constant pH during irradiations. Absorbance of borate solution in the range 300–600 nm was corrected prior to measurements with ADPA–PECA and ADPA–fluorescein pairs. The concentration of PECA was in the range of 10–25 ppm (0.010–0.025 mmol) and the concentration of ADPA was kept at about 10 ppm (0.01 mmol) for all studies in distilled water solutions. Ferric chloride was supplied by Fluka, and used without any purification.

3. Results and discussion

Synthesized PECA gives a pink-red colour in aqueous solutions. A striking difference for the absorptions of PECA is observed in aqueous solutions (Fig. 1). The characteristic λ (ε): 458 (17 600)–490 (42 100)–526 (57 600) nm triple absorptions of all the known perylene diimides in organic solvents, is found to shift to shorter wavelength, about 50 nm, and the molar absorbtivities decreased, λ (ε): 407 (7200)–438 (14 900)–466 (18 800), in water. Enhanced hydrogen bonding interactions in water, probably have caused an increase of $n-\pi^*$ energy level gap. This difference corresponds to an increase in singlet energy of perylene diimides. The fluorescence quantum yields of perylene diimides are reported to be near unity in organic solvents. The fluorescence emission intensity of PECA in Fig. 2 is seen to be pH dependent. The cause of decrease of fluorescence
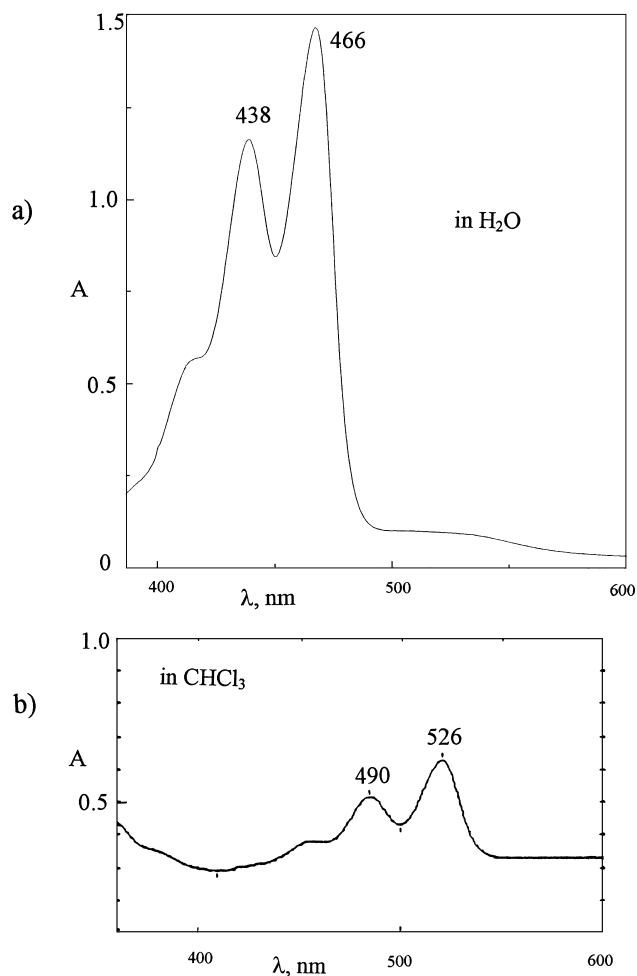

Fig. 1. UV absorbtion spectra of perylene 4-carboxylphenyl-*bis*-diimide (PECA): (a) in water at pH 6.90, and (b) in chloroform.
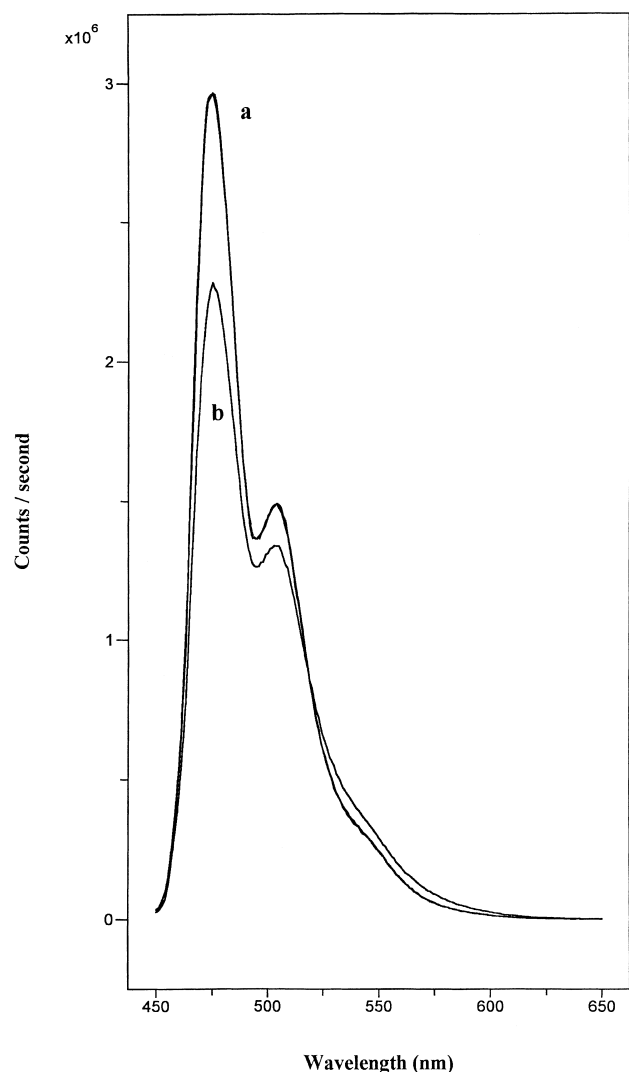
Fig. 2. Fluorescence emission spectra of perylene 4-carboxylphenyl-*bis*-diimide (PECA), λ_{exc}=438 nm, in water: (a) at pH 11.85, and (b) at pH 6.60.

emission of PECA in the order of pH values 11.85–6.60 is attributed to the aggregation effect. A supporting evidence is detected in UV absorptions that the most intense band at 466 nm decreased about 20% from pH 13 to 6, at repeated trials. Decreasing solubility at lower pH values would cause the formation of aggregates that may result in intermolecular energy transfer, observed previously as concentration quenching [14], and overall observation would

be the decline of fluorescence mission. Calculation of the fluorescence quantum yield of PECA (λ_{exc}=438 nm) with reference to the fluorescence emission of fluorescein in ethanol ($Q_f^{fluorescein} = 0.97$) yielded the following values:

pH : 11.85–6.60
Q_f^{PECA} : 1.0–0.86

The fluorescence quantum yield of PECA in chloroform was found to be 0.87, with reference to *n*-dodecyl perylene diimide (Q_f=1.0 [9]) as seen in Table 1. The radiative lifetimes, τ_0, were calculated by the formula [14,15]: $\tau_0 = 3.5 \times 10^8/(\nu_{max}^2 \, \varepsilon_{max} \, \Delta\nu_{1/2})$, where ν_{max} is the wavenumber per centimetre, ε_{max} the molar extinction coefficient at the selected absorption wavelength, and $\Delta\nu_{1/2}$ the half width of the selected absorption in wavenumber unit (cm^{-1}). Fluorescence lifetimes are estimated as τ_f=$\tau_0 Q_f$ and the rates of fluorescence as k_f=1/τ_0 in Table 1. In neutral aqueous solution, the radiative and fluoresence lifetimes of PECA are seen to be enhanced about twice, and the rate of fluorescence emission declined by the same ratio. The enhancement of singlet energy of PECA by 7 kcal mol^{-1}, in water, is expected to cause the variation of photochemical reactivities with respect to the organic phase.

3.1. Fluorescence quenching with cobalt ions

Quenching of fluorescence emission studies show that perylene diimides behave as electron acceptors toward π-electron rich aromatics of carbazolocarbazole, phenanthrene and even naphthalene [16] in organic solvents, but behave as an electron donor toward acceptor Co^{+2} ions [7] in alcohols. Although the singlet energy level is found to be slightly high in aqueous solution (ΔE_s=7 kcal mol^{-1}), PECA is expected to present similar fluorescence quenching in water. Fluorescence emission quenching of PECA was studied at increasing concentrations of cobalt ions, CoCl$_2$, (0–14)$\times 10^{-6}$ M, at pH 8.5 in water. A Stern–Volmer plot (Fig. 3) yielded a quenching rate, k_q, of 2.3$\times 10^{12}$ M^{-1} s^{-1}. The Stern–Volmer plot deviated from linearity above concentrations of 1.36$\times 10^{-5}$ M. Therefore calculations are carried out in concentration range of (0–1.36)$\times 10^{-5}$ M. Fluorescence lifetime, τ_f, of PECA in water is taken to be 15.0 ns in calculations (Table 1). El-Daly [7] reports the rate of quenching of perylene di-*t*-butylphenyldiimide with cobalt ions in methanol, at diffusion rate limit of k_q=1$\times 10^{10}$ M^{-1} s^{-1}. This value is about 100-fold smaller.

Table 1
The UV absorption data of PECA in chloroform and aqueous solutions (at pH=6.0)[a]

Solvent	λ_{max} (nm)	ε_{max} (l mol^{-1} cm^{-1})	Q_f	τ_0 (ns)	τ_f (ns)	$k_f \times 10^8$ (s^{-1})	E_s (kcal mol^{-1})
CHCl$_3$	526	57600	0.87	9.3	8.1	1.1	54.4
H$_2$O	466	18800	0.86	17.5	15.0	0.6	61.4

[a] Wavelength: λ_{max}, molar absorbtivity constant: ε_{max}, fluorescence quantum yields: Q_f, radiative lifetimes: τ_0, fluorescence lifetimes: τ_f, fluorescence rate constants: k_f, singlet energies: E_s.
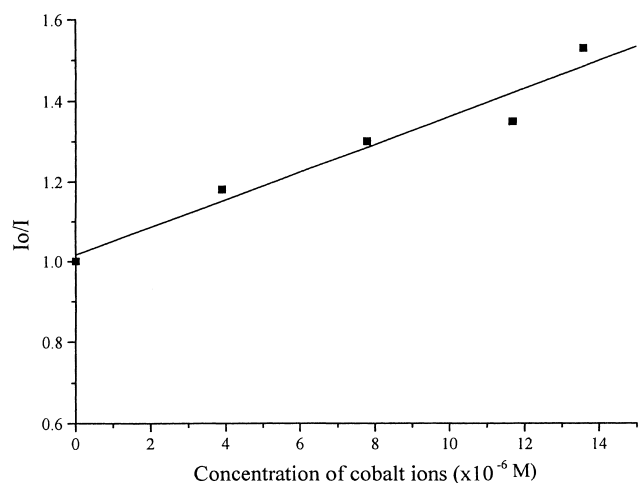
Fig. 3. Stern–Volmer plot for fluorescence quenching of perylene 4-carboxylphenyl-*bis*-diimide (PECA), λ_{exc}=438 nm, in the presence of increasing concentrations of CoCl$_2$, (0–13.6)×10^{-6} M, in water at pH 8.5.

On the other hand, the quenching rates of perylene *bis*-dodecyldiimide with π-electron donors, are reported to be above diffusion rate limits, 10^{11}–10^{14} [16]. Static quenching, in addition to dynamic quenching is attributed to the observation of high quenching rates with perylene diimides by π-electron donors. High quenching rates point to the tendency of photo-electron transfer with perylene diimides. This tendency has been proven by the detection of perylene diimide anion radical and superoxide anion radical in organic solvents of an ESR spectroscopy, flash photolysis and transient UV absorption studies [10,11]. The present result of high fluorescence quenching rate in water may be attributed a similar electron transfer mechanism for aqueous solutions.

3.2. Superoxide/hydroperoxy quantum yields

Perylene diimides are proven to produce superoxides on irradiation [10,11] in the presence of an olefin, i.e. α-terpinene. The presence of superoxide anion radical
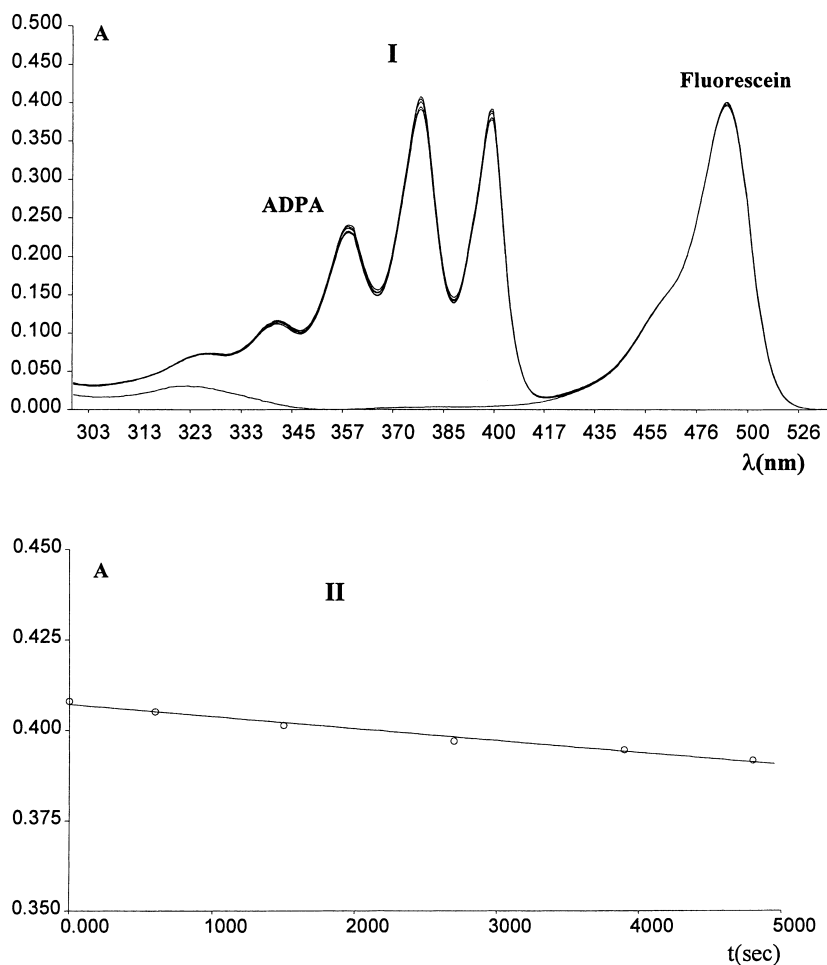

Fig. 4. (I) The spectra on the decline of ADPA (10 ppm) absorbance versus time in the presence of fluorescein (25 ppm) in water at pH=9 (borate buffer) and under irradiation at 378 nm. The spectra are corrected for a constant absorbance of fluorescein. (II) The plot on the decline of ADPA absorbance versus time in the presence of fluorescein ($\phi_{^1O_2}^{fr}$ = 0.032 [16]).
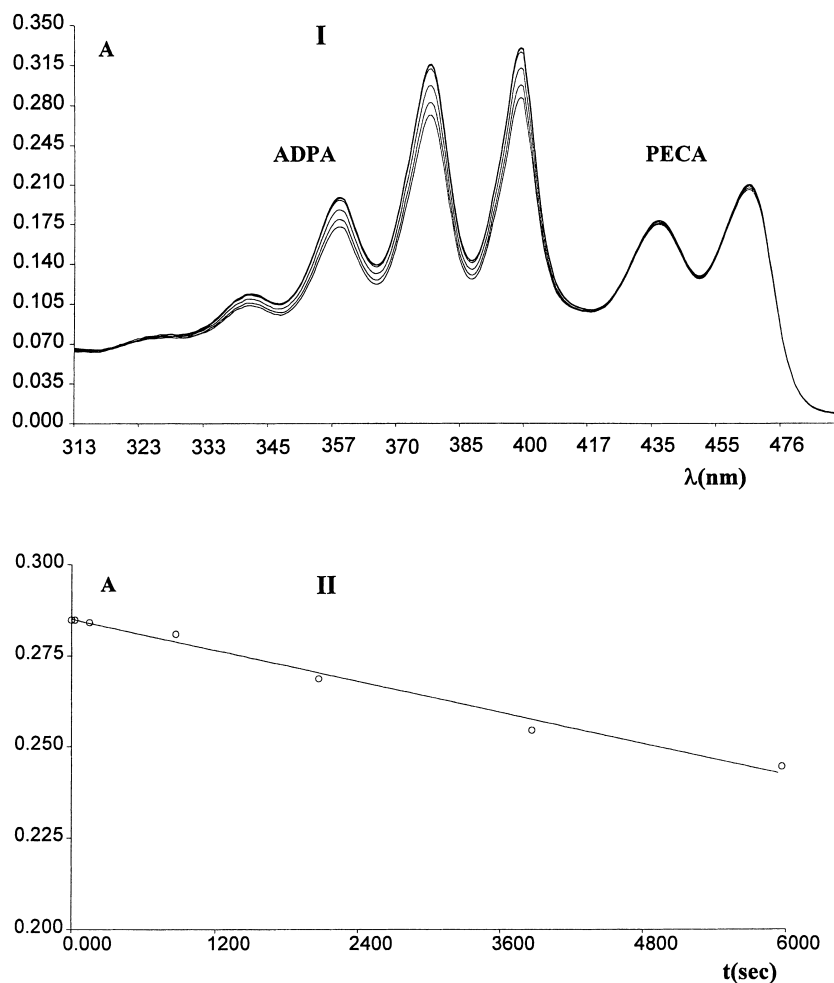
Fig. 5. (I) The spectra on the decline of ADPA (10 ppm) absorbance versus time in the presence of PECA (25 ppm) in water at pH=9 (borate buffer) and under irradiation at 465 nm. The spectra are corrected for a constant absorbance of PECA. (II) The plot on the decline of ADPA absorbance versus time in the presence of PECA ($\phi^{PECA}_{{}^1O_2{}^{\bullet-}} = 0.062 \pm 0.012$).

($O_2{}^{\bullet-}$) and protonated superoxide-hydroperoxy radical ($HOO^\bullet$) is proven in the presence of perylene *N*-phenyl *bis*-diimide on photooxidation of α-terpinene [10,11] and abietic acid [11]. It is evident that photooxidation processes of perylene diimides proceed via the intermediates that form on electron transfer from perylene diimide anion radical to oxygen. However, quantum yields of this process have not been reported. In order to be able to determine the superoxide and/or hydroperoxy quantum yields in aqueous phases, 9,10-anthracene-dipropionic acid (ADPA) has been synthesized. Rodgers [17] has developed a method for the calculation of singlet oxygen quantum yields based on the formation of ADPA-endoperoxide adduct by detection of loss of UV absorption of ADPA.

ADPA   (λ_{abs} = 400 nm)   ADPA-Adduct
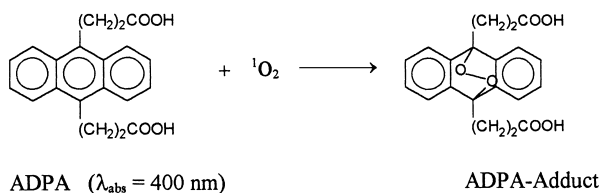
It is expected that superoxide anion radical or protonated equivalent hydroperoxy radical would also react with ADPA and resulted in loss of UV absorption of ADPA, as observed in the experiments. Superoxide/hydroperoxy radical quantum yield of PECA in the presence of ADPA, was estimated by the application of Rodgers method. Calculations were done in reference to singlet oxygen quantum yield of fluorescein in water ($\phi^{fr}_{{}^1O_2} = 0.032$ [18]), by using the formula:

$$\phi^{PECA}_{O_2{}^{\bullet-}} = \phi^{fr}_{{}^1O_2}\left(\frac{m^{PECA}}{m^{fr}}\right)\frac{[A]^{fr}}{[A]^{PECA}}$$

The m^{PECA} and m^{fr} are the slopes of ADPA absorbance decline respect to time in the presence of PECA and fluorescein, respectively (Figs. 4 and 5). Fluorescein is selected since its absorbance is in the same region as that of PECA. Monochromatic light of PTI QM1 emission spectrophotometer at 465 nm was used for both experiments. The absorbances of PECA and fluorescein were kept constant in corrected spectra for calculations (Figs. 4 and 5), while the
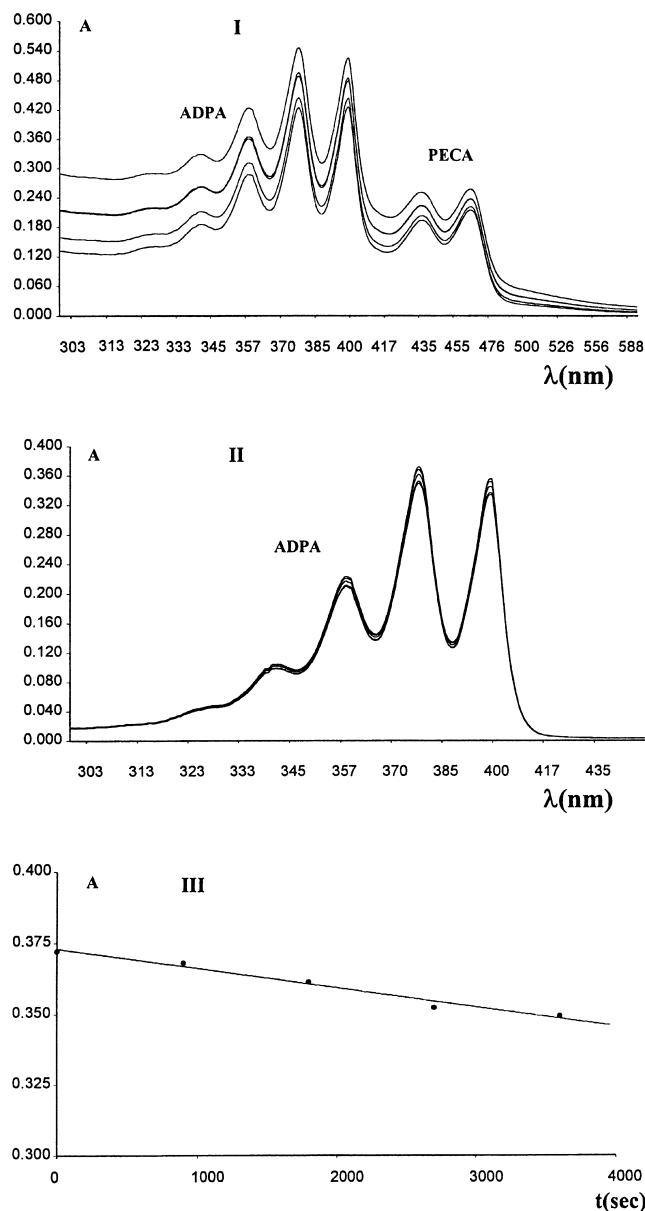
Fig. 6. (I) The experimental spectra on the decline of ADPA (10 ppm) absorbance versus time in the presence of PECA (25 ppm) and ferric ions (100 ppm) in water at pH=9 (borate buffer) and under irradiation at 465 nm. (II) ADPA absorbance spectra are corrected for a constant absorbance of PECA. (III) The plot on the decline of ADPA absorbance versus time in the presence of ferric ions and PECA ($\phi_{O_2^{\bullet-}}^{PECA/Fe} = 0.093$).

absorbance of ADPA declined on photooxidation. Superoxide/hydroperoxy radical quantum yield of PECA, $\phi_{O_2^{\bullet-}}^{PECA}$, is estimated to be 0.062±0.012 at pH 9.

The addition of ferric ions into the solution of the PECA–ADPA pair resulted in an increase of about 50% of superoxide/hydroperoxy quantum yields, below 0.1 mmol (100 ppm) concentrations (Fig. 6). Above these concentrations, superoxide/hydroperoxy quantum yield decreased together with a precipitation in solution (probably precipitation of ferric and/or ferrous hydroxide). Ferric ions

were expected to increase the rate of formation of superoxide/hydroperoxy oxidative intermediate by an additional electron transfer mechanism.

Quantum yield values in water were seen to be low. But the reported high quantum yield of oxidation, 0.4, for α-terpinene photooxidation in the presence of N-phenyl perylenediimide in acetonitrile [10,11] indicates an effective pumping of superoxide/hydroperoxy photooxidation and unusual high stability of perylenediimide anion radical intermediate.

3.3. Photodegradation of pesticides in water

Thorough photooxidation of α-terpinene and monoterpene abietic acid [19] in acetonitrile suggests that organic contaminants, such as pesticides can be degraded to oxygenated products in the presence of perylene diimide under sun light. Bromacil pesticide is reported to be converted to hydantoin derivatives on singlet oxygen photooxidations by the use of methylene blue (MB) photosensitizer [5]. Absorption band of bromacil at 278 nm in oxygenated MB aqueous solution, is detected to decline to about 70% intensity, and then the absorption begins to build up due to increasing concentration of hydantoin products. HPLC studies revealed that complete degradation of bromacil is being reached shortly after the curving of 278 nm absorption band [4]. A similar work is now conducted with PECA under 400 W sodium lamp irradiation, i.e. equivalent to 1 sun solar irradiation. Fig. 7 shows that little degradation of 300 ppm bromacil is detected in the presence of 10 ppm PECA — in the absence of oxygen (deaerated), and in the absence of PECA — in the presence of oxygen (aerated), respectively, at pH 6.5. Partial degradation (estimated: 50% degradation, compared to degradation by MB under the same conditions) of 300 ppm bromacil in 1 h at pH 8.5, is seen when 10 ppm of PECA and oxygen are present (Fig. 7). It is apparent that the superoxide of PECA degrades the bromacil pesticide, but not as effective as the singlet oxygen, produced by MB.

Complete solar degradation of bromacil with ferric ions in the photo-fenton reaction is reported [10,11], but only in highly acidic aqueous solutions (pH: 1–3). Hydroxyl radicals, are known to degrade the organics in aqueous solution in the photo-fenton reaction. Hydroxyl radicals are not expected to be produced in neutral and basic aqueous solutions. In agreement with this, no degradation of 300 ppm bromacil is detected in the presence of only 12 ppm FeCl₃ at pH 6.5. But a satisfactory result with bromacil is observed in the presence of catalytic amounts of PECA (10 ppm) and ferric ions (12 ppm), under sodium lamp illumination at pH 6.5 and pH 8.5 (Fig. 7). The curve is similar to the degradation of bromacil in the presence of MB, which points to a complete degradation of bromacil.

2,4-Dichlorophenoxyacetic acid (2,4-D) pesticide, a commonly used agricultural pesticide in Turkey, has been
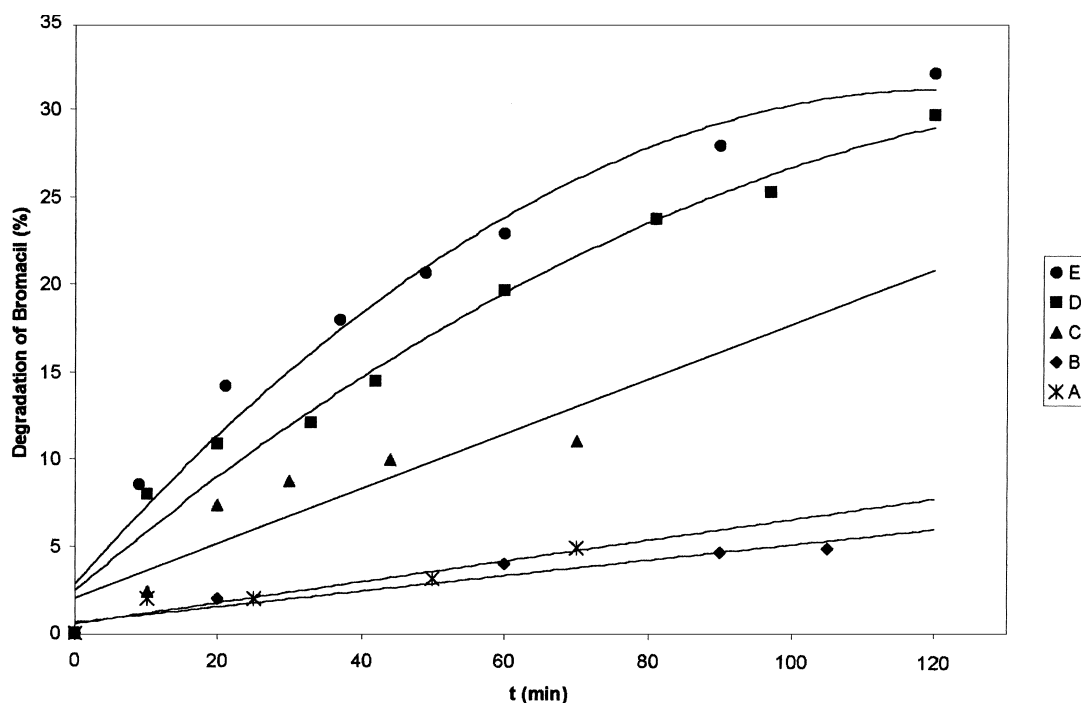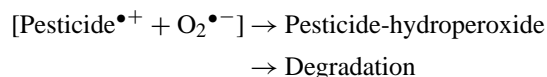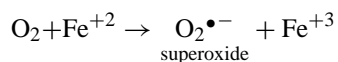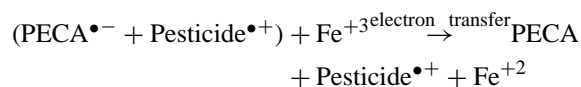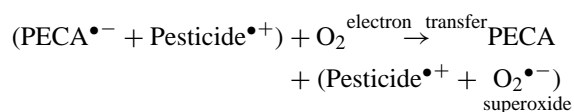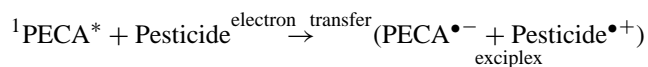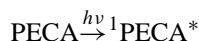
Fig. 7. Plots for quenching of absorbance of bromacil (300 ppm) at 278 nm versus time (minutes) under irradiation with a 400 W sodium lamp and in the: (A) presence of 10 ppm PECA in deaerated solution (pH 6.5); (B) absence of PECA in aerated solution (pH 6.5); (C) presence of 10 ppm PECA in aerated solution (pH 8.5); (D) presence of 10 ppm PECA and 12 ppm ferric ions in aerated solution (pH 8.5); (E) presence of 10 ppm PECA and 12 ppm ferric ions in aerated solution (pH 6.5).

treated with PECA/Fe^{+3} (10 ppm PECA, 13 ppm FeCl$_3$) at 1000 ppm concentration. The loss of pesticide is followed by the absorption of 2,4-D at pH 6.5, at 284 nm (Fig. 8). Degradation is completed in 5 h. This result may present a novel photo reaction mechanism for perylene diimides in aqueous solutions:

$$\text{PECA} \overset{h\nu}{\rightarrow} {}^{1}\text{PECA}^{*}$$

$$^{1}\text{PECA}^{*} + \text{Pesticide} \overset{\text{electron transfer}}{\rightarrow} \underset{\text{exciplex}}{(\text{PECA}^{\bullet-} + \text{Pesticide}^{\bullet+})}$$

$$(\text{PECA}^{\bullet-} + \text{Pesticide}^{\bullet+}) + \text{O}_2 \overset{\text{electron transfer}}{\rightarrow} \text{PECA}$$
$$+ \underset{\text{superoxide}}{(\text{Pesticide}^{\bullet+} + \text{O}_2^{\bullet-})}$$

$$(\text{PECA}^{\bullet-} + \text{Pesticide}^{\bullet+}) + \text{Fe}^{+3} \overset{\text{electron transfer}}{\rightarrow} \text{PECA}$$
$$+ \text{Pesticide}^{\bullet+} + \text{Fe}^{+2}$$

$$\text{O}_2 + \text{Fe}^{+2} \rightarrow \underset{\text{superoxide}}{\text{O}_2^{\bullet-}} + \text{Fe}^{+3}$$

$$[\text{Pesticide}^{\bullet+} + \text{O}_2^{\bullet-}] \rightarrow \text{Pesticide-hydroperoxide}$$
$$\rightarrow \text{Degradation}$$

Ferric ions probably enhance the production rates of both pesticide cation radical and the superoxide anion radical, that would result in enhanced degradation reactions.

Photocatalyzed degradation rates of phenol by TiO$_2$ is most efficiently determined by the measurement of phenol fluorescence emission at excitation wavelength of 268 nm [20]. Similar experiments are done in the presence of phenol (10^{-4} M), PECA (5–10 ppm), FeCl$_3$ (1–20 ppm) in pH range of 6.5–11.0 [Fe(OH)$_3$ was precipitated in alkaline solution, and filtered out prior to emission studies]. No decline of fluorescence emission of phenol at 268 nm excitation wavelength was detected under radiation, in durations of 2–16 h. In order to confirm the results, another phenol derivative *o*-nitrophenol, was selected, for which the fluorescence emission wavelength is different from the fluorescence emission wavelength of phenol. The experiment was repeated with *o*-nitrophenol, and the fluorescence emission at 316 nm excitation wavelength was examined. Again no reactivity was detected. These results suggest that the photooxidation capability of superoxide anion radical or hydroperoxy radical, as that of singlet oxygen, is unable to degrade a stable aromatic ring structure such as in phenol.

The reactivity of 2,4-D pesticide with PECA/Fe^{+3} solar photocatalyst, may be attributed to an attack of superoxide on the carboxylic acid moiety, that results in degradation of the substituted chain on the benzene molecule, which is followed by 284 nm absorption.
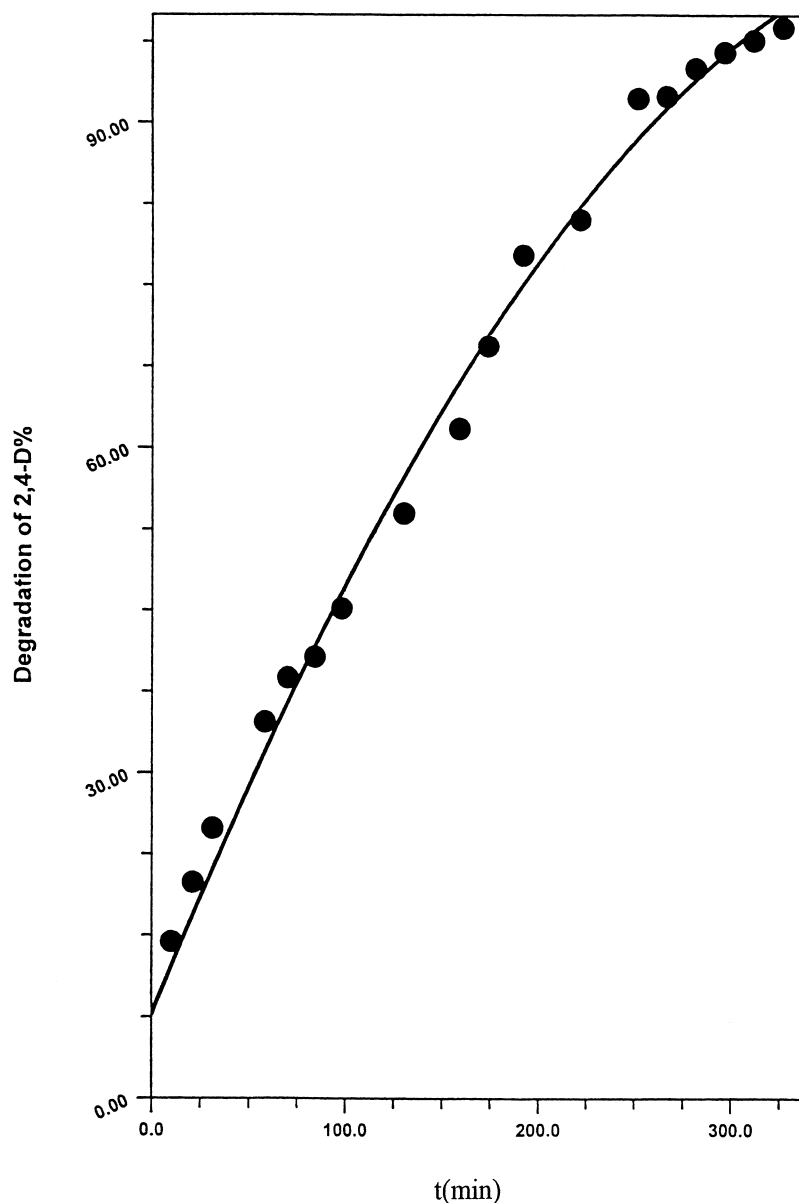
Fig. 8. Plot for quenching of absorbance of 2,4-D pesticide (1000 ppm) at 284 nm versus time (minutes) under irradiation with 400 W sodium lamp, and in the presence of 12 ppm ferric ions, 10 ppm PECA, in aerated aqueous solution (pH 6.5).

4. Conclusions

Synthesized water soluble PECA, is proven to produce reactive superoxide anion and/or hydroperoxy radical in neutral to basic aqueous solutions, as in organic solvents, in spite of the singlet energy of PECA being 7 kcal mol^{-1} higher in water, with respect to the singlet energy in organic phases. The quantum yield of fluorescence emission, Q_f, was measured to be 1.0 at pH 11.85, and 0.87 at pH 6.60. The difference is attributed to an aggregation effect due to low solubility in neutral aqueous solution, as detected in organic phase studies of perylene diimides. A fluorescence quenching with Co^{+2} ions has yielded the high quench-

ing rate of $2.3 \times 10^{12} \, M^{-1} \, s^{-1}$ for PECA fluorescence emission, taken as evidence for singlet electron transfer. Degradation of bromacil and 2,4-D pesticides in neutral aqueous solutions in the presence of catalytic amounts of PECA and ferric ions, has proven that PECA/Fe^{+3} solar photocatalyst is as reactive as singlet oxygen photooxidations for organic pollutants, and has the following advantages:

1. stability and durability of catalysts under solar irradiation;
2. removal and regain of catalysts by simple precipitation, in acidic solutions of PECA, and in basic solutions of ferric ions.

Similar to singlet oxygen, the PECA/Fe^{+3} pair could not degrade stable aromatic structures, such as phenol under solar irradiation conditions.

Acknowledgements

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